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PILOT-SCALE INVESTIGATION OF CLOSED-LOOP FLY ASH SLUICING:

VOL. 1 - FINAL REPORT

by:

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16. ABSTRACT The report gives results of a pilot-scale demonstration of the technical feasibility of closed-loop operation of fly ash sluicing systems. Chemical species leached from the ash increase the dissolved solids concentration of recycled sluice water to a point where equipment scaling may occur. Tests were conducted at two power plants using a 50-gpm pilot unit to demonstrate the feasibility of closed-loop operation, both with and without sluice water treatment. An ash sluice computer process model was developed to predict chemistry and process conditions in full-scale systems. Fly ash sluicing systems handling highly reactive alkaline ashes cannot be operated closed-loop without treating the sluice water to control scale formation. Adding acid to adjust pH was effective in controlling calcium carbonate scale formation in the sluice water return line; however, it increased the potential for gypsum scale formation. Gypsum was ultimately the limiting species which prevented reliable closed-loop operation at the plants tested. Increased ash/water contact time in a reaction tank was not adequate to control the potential for gypsum scale formation at the residence time tested. The ash sluice computer process model proved to be accurate in predicting the chemical composition and potential for scale formation in the pilot unit.

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ABSTRACT

In order to address potential impacts of closed-loop operation on power plant ash sluicing systems, the U.S. EPA conducted a series of three projects designed to identify potential chemistry-related operating problems and to test several control approaches. Results of the first project indicated that closed-loop operation of fly ash sluicing systems requires some form of treatment to control scale formation. Treatment options considered included 1) pH adjustment, 2) greater solids retention time to allow precipitation, and 3) sidestream softening. Due to the variability and developmental nature of the computer model used in the evaluation, additional bench- and pilot-scale studies were recommended.

In response to the recommendations of the first project, two additional projects were initiated. In the first of these, funded by EPA's Effluent Guidelines Division, the ash sluice systems at three power plants were characterized. The second project, the subject of this report, involved the design, construction, and field testing of a pilot unit and use of the acquired field data to evaluate the ash sluice process model. Data collected during the field tests were used to evaluate the feasibility of closed-loop operation and to refine the predictive capability of the ash sluice computer process model.

Results of this study indicate the model to be an effective tool for predicting chemical composition and scale formation potential, provided accurate input data are available. Critical inputs to the model that can significantly affect the accuracy of the model predictions include 1) ash leaching data, 2) the quantity of CO_2 transfer in the ash ponds, and 3) estimates of the potential for precipitation in ash sluice equipment. Results of the program indicate that laboratory ash leaching data are adequate to use as inputs to the model.

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SECTION 1

INTRODUCTION

Increased concern over the discharge of wastewater streams containing priority pollutants has focused attention on ash sluice water systems in coal-fired power plants. Inorganic priority pollutants can be leached from fly ash and bottom ash along with other soluble species (primarily calcium, magnesium, sodium, chloride, and sulfate) by the sluice water used to slurry these materials to settling ponds or disposal systems. Ash sluicing to disposal is a common practice in the utility industry.

Conceptually, there are two fundamental approaches to eliminating the direct discharge of priority pollutants from ash sluicing systems:

- dry-convey the ash to final disposal, and
- recycle/reuse the water currently being discharged for ash sluicing.

The first approach would be more easily implemented in the design of new facilities but may not be practical for existing plants. The second approach attempts to confine all chemical species in a "closed" system. Closed-loop or zero discharge operation of ash sluice water is practiced at only a few facilities. Consideration of this mode of operation may be necessary for plants with coal ashes containing significant quantities of leachable pollutants.

This report summarizes the results of an EPA program to demonstrate the technical feasibility of closed-loop ash sluicing on the pilot-scale. This program included the design and construction of a pilot unit to simulate full-scale plant operating conditions, field testing at two power plants, and the development of a computer model to simulate an ash sluice system. This report describes the pilot feasibility tests and documents the current status of computer model development, including field validation, and information required to use the ash sluice process simulation model.

The remainder of this section describes the program background, objectives, and schedule. Section 2.0 summarizes the results of the laboratory and field simulation testing and compares these results with the predictions of the computer simulation model. A user's manual for the ash sluice process computer simulation model is found in Section 3.0. A description of the pilot system, the field test program, and the results of the testing and the computer process model predictions are included in Section 4.0.

1.1 BACKGROUND

The combustion of coal to generate electric power produces large quantities of ash requiring disposal. Larger ash particles are collected in the bottom hopper of the boiler while the lighter particles, fly ash, are carried out of the boiler by the combustion gases. The larger particles of the fly ash are collected in the boiler economizer hoppers or by mechanical collectors and are referred to as economizer ash. The finer particles are collected downstream of the economizer by electrostatic precipitators, baghouses, or wet scrubbers. Typically, the fly ash stream is the largest ash stream produced from the combustion of coal in a utility boiler. Economizer ash represents only a very small fraction of the total ash produced. As a result economizer ash is generally disposed of with either the fly ash or the bottom ash streams.

Several methods are commonly used for disposal of bottom ash and fly ash after collection. The first method involves the transport of dry ash to its final disposal site with only limited exposure to the atmosphere. This method is commonly used for fly ash disposal and, in some cases, for bottom ash disposal. The second method involves the use of water to convey both bottom ash and fly ash from the plant to an ash pond or some other storage/dewatering system. Bottom ash sluicing is a common practice in the electric utility industry while fly ash sluicing is practiced to a lesser extent. Ash ponds are often used as the final disposal site for both bottom ash and fly ash. The ash usually settles to the pond bottom rapidly, producing a clarified water which is often discharged to a nearby stream or river. Information collected under EPA Contract No. 68-02-2608, Task 66, indicates that approximately 40 percent of power boiler installations in the United States sluice fly ash on a once-through basis with no recirculation or reuse of the sluice water (1). A third method of fly ash disposal available to those plants with flue gas desulfurization (FGD) systems is the blending of fly ash with scrubber sludge. This blending can be accomplished in a variety of ways. For example, simultaneous removal of fly ash and SO_2 in a common system produces a sludge that is often ponded. Or, dry fly ash may be blended with FGD sludge (with or without chemicals) to stabilize the sludge for landfill disposal. The leaching of soluble species from these combined disposal methods was not within the scope of this program.

The selection of the method of disposal is dependent on the coal burned (ash fusion properties), boiler design, availability of water, plant site factors, and applicable regulations. For example, where water supply is limited or where the plant is located at the coal mine, dry fly ash handling is often the best approach to fly ash disposal. These options must be evaluated on a site-by-site basis in order to develop the most economic approach to ash disposal.

The intimate mixing of power plant ash and water during sluicing causes soluble species (such as calcium, chloride, sulfate, sodium, and trace elements) to be leached from the ash. An increase or decrease in the pH level can also result, depending on the characteristics of the coal ash. The discharge of pond water containing high levels of these dissolved species at low or high pH and suspended ash is an environmental concern. In most cases, fly ash has been found to contain greater quantities of leachable species than bottom ash in sluicing systems. Fly ash is also produced in much greater quantities at electric utility plants. For these reasons, control of discharges from fly ash sluicing systems has been an environmental concern for some time. Two options are available to the plant operator or designer for elimination of discharges from fly ash sluicing: dry fly ash handling and disposal and closed-loop operation of wet ash sluicing systems. Dry fly ash handling and disposal is expected to be used in the design of most new coal-fired power plants. Closed-loop (zero discharge) operation of fly ash sluicing systems has not been a common practice in the utility industry. To achieve closed-loop operation these systems will be required to use more concentrated water with higher TDS levels which result from additional contact between fly ash and recycled ash sluice water.

Recycling of ash pond water to create a closed-loop ash sluicing system can cause many operating problems. Scale formation in various areas of an ash sluicing system is one of the major concerns in closed-loop operations. Calcium, magnesium, sodium, sulfate, and silica are the major species leached from the fly ash and subsequently concentrated due to the recycle. Concentration of these soluble species in a closed-loop system can cause the sluice water to become supersaturated with respect to calcium carbonate ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$), magnesium hydroxide ($Mg(OH)_2$), or silica compounds, resulting in precipitation and the potential for scale formation on surfaces in certain parts of the system. Failure to control the buildup of scale-forming compounds in the ash system by various treatment approaches may result in plugging of piping, pumps, hydrovactor and other portions of the system where elevated temperatures may be encountered. This scaling can significantly impact the reliability of the ash sluice system, thus impacting the availability of the generating unit.

In order to address the potential impacts of closed-loop operation of power plant ash sluicing systems, the EPA has conducted a series of projects directed at defining potential chemistry-related operating problems and testing of several control approaches. The first of these projects was summarized in "Water Recycle/Reuse Alternatives in Coal-Fired Steam Electric Power Plants," EPA Contract No. 68-03-2339. This project was conducted for EPA's Industrial Environmental Research Laboratory in Research Triangle Park, North

Carolina (IERL-RTP), in 1978 (2). During this project, water samples from cooling towers, ash sluicing, and sulfur dioxide and particulate scrubbers at five power plants in different regions of the country were collected and analyzed. The results of these analyses were then evaluated using a computer process model to determine the reuse potential of each stream and identify alternatives for minimizing water requirements and discharges for each plant. This study indicated that closed-loop operation of fly ash sluicing systems would require treatment to control scale formation. Treatment options considered in this study included 1) pH adjustment, 2) greater solids retention time to allow precipitation, or 3) sidestream softening. The treatment requirements for each plant were highly variable due to the different leaching characteristics of the ash. Because of the variability and developmental nature of the computer model used in the evaluation, additional bench- and pilot-scale studies were recommended. These studies would be used to further define ash leaching characteristics and confirm/improve the accuracy of the model using data from simulated full-scale plant operating conditions.

In response to the recommendations of the above study, two additional EPA projects were initiated. The first was funded by EPA's Effluent Guidelines Division in 1979 under EPA Contract 68-01-5163, Task 8. In this project, three power plants were selected and the ash sluice systems at each plant were characterized. This characterization included a review of design operating conditions, collection of fly ash and bottom ash and sampling/analysis of sluice, makeup, and pond effluent waters. The ash collected in the field was used in a bench-scale simulation of a closed-loop ash system to evaluate ash leaching and dissolved solids buildup. A technical note discussing the results of this program is presented in Appendix E. These data were used to refine the accuracy of the ash sluice system computer simulation model.

Near the conclusion of the above project, IERL-RTP began to develop a pilot-scale fly ash sluicing system to allow field testing under realistic plant operating conditions under EPA Contract 68-02-3163. The design of the pilot system incorporated the plant operating and bench-scale data collected in the previous program to ensure that the full range of expected fly ash sluicing system operating conditions could be simulated. The data collected during the field tests would be used to evaluate the feasibility of closed-loop operation and to refine the predictive capability of the ash sluice process computer model. The field test data and ash sluice process model are the focus of this document and will be discussed in detail in later sections.

The result of these three EPA projects has been the development and validation of a computer process simulation model that can predict ash sluice system water chemistry and scaling potential, and that can be used for evaluating the potential of various treatment approaches to control scale formation. The simulation model was developed to use laboratory ash leaching data, makeup water composition, and ash sluice system design and operating conditions to predict the full-scale system chemistry conditions. This will allow designers of new systems and operators of existing systems the opportunity to determine the potential for severe scaling, evaluate control options, and develop system operating guidelines based on a minimal amount of chemistry and process data. The need for pilot-scale testing to define the scaling tendency/potential in the ash sluice system before startup would be minimized. The simulation model is also useful in evaluating and developing solutions to scaling problems in existing ash sluicing systems.

1.2 PROJECT OBJECTIVES

The primary objective of this project is to investigate the technical feasibility of closed-loop operation of fly ash sluicing systems. To achieve this objective, three major tasks were completed:

- development, design, and construction of a pilot-scale system to simulate full-scale system operating conditions,
- field testing with the pilot system to investigate the feasibility of closed loop mode operation, and
- development/verification of the ash sluice process simulation model using field data.

The objectives of each of these activity areas will be discussed in the following paragraphs.

Development and design of the fly ash pilot system were based on data from full-scale ash sluicing systems and bench-scale studies. The objectives of this task were:

- to develop a system design that would duplicate a range of flow and mixing conditions found in plant systems,
- to design and construct a system that was easily transportable and adaptable to several plant locations, and
- to develop a system that could demonstrate various treatment alternatives to reduce the potential for scaling.

The system required a high degree of flexibility to allow operation at various slurry concentrations and provide three treatment approaches for scaling control that could be evaluated. These treatment approaches included: 1) pH adjustment, 2) softening of the ash recycle water, and 3) increased mixing time for fly ash slurry to encourage precipitation on the ash particles.

Field testing was conducted to provide a broad process and chemistry data base. This was to be accomplished by testing at several power plants to provide a broad data base of chemistry and operating conditions. The objectives of this task were to:

- develop representative process and analytical data at steady-state operating conditions,
- demonstrate the feasibility of reducing ash system blowdown to zero (i.e., a closed-loop mode of operation), and
- demonstrate the potential of three treatment approaches to control scale.

The field test plan was closely correlated with the data requirements of the process simulation model to ensure that all key parameters were evaluated.

The final task involved the comparison of process and chemistry data collected in the field with the results of the computer model. The objectives of this task were to:

- confirm the accuracy of the model in predicting the pilot system chemistry and operating conditions,
- identify the sensitivities of the model to operating parameters such as ash leaching rate and slurry concentration,
- confirm the effectiveness of the treatment alternatives,
- upgrade the model, where required, to more closely simulate the process, and
- relate the field test data and model predictions to the full-scale plant system.

This task documents the status of the process simulation model and the level of confidence that could be placed in the model's predictions for a full-scale system.

1.3 PROJECT DESCRIPTION

In order to evaluate the feasibility of closed-loop ash sluicing, the project was divided into three major task areas:

- pilot unit design and construction,
- test plan development, and
- field evaluation of closed-loop operation.

The first area involved the design, equipment acquisition, and construction of the pilot system. The final two areas involved the development of a comprehensive test plan for each test site, transportation and set-up of the systems, and the execution of the plan in the field. To better understand the project activities, each task will be described briefly.

1.3.1 Pilot Unit Design

In the development of the pilot system, the following steps were completed:

- preparation of process and instrumentation drawings;
- preparation and issuance of bid specifications, selection of vendors, and procurement of equipment; and
- construction of the pilot unit.

An operating manual was developed and verified in the field. This manual contains all the pertinent start-up, operation, and shutdown procedures used along with the control modes of each tank and pump. A copy of the operating manual is included in Appendix I. All equipment maintenance data were also compiled in a manual. This manual provided equipment purchase orders, recommended spare parts lists, and contained maintenance procedures and operating limits for all equipment items.

1.3.2 Test Plan Development

Test plans were prepared for operation of the pilot unit at each of the two participating plants. These were submitted to the EPA Project Officer and the applicable utility for review. Copies of test plans are included in Appendix F and Appendix G. Each test plan contained the following:

- specific operating conditions and duration for each test to be conducted;
- sample points, frequency of sampling, and liquid and solid analyses to be performed for each sample;
- data sheets and procedures for reducing the data for purposes of modifying the computer model; and
- quality control and quality assurance procedures.

The computer model was used in conjunction with data collected under EPA Contract 68-01-5163, Task 8, to determine treatment requirements as a function of degree of recycle in order to anticipate operating characteristics and to specify operating conditions for the pilot unit at each site. The technical note summarizing this project is included in Appendix E.

1.3.3 Field Evaluation of Closed-Loop Operation

The pilot unit was operated at two plant sites to determine if closed-loop operation could be achieved. The pilot system was operated at slurry concentrations ranging from 3 to 10 weight percent solids. The chemistry of the sluice water at various points in the sluicing system was characterized on site. The chemistry and process data collected in the field were entered in the ash sluice simulation model to determine the blowdown rate for the next test condition. Where total recycle was not possible without scale formation, the effectiveness of the following treatment alternatives to control scale and increase recycle were evaluated:

- sidestream softening of the recycle water,
- pH adjustment of the recycle water, and
- providing adequate reaction time (by means of a tank) prior to slurrying the ash to the pond.

The specific operating conditions, sample points and analyses, and test duration at each of the plant sites are specified in the test plans included in Appendix F and Appendix G. The results of these tests and correlations with the process simulation model are compiled in later sections of this report.

1.4 PROJECT SCHEDULE

This project was started in November 1979 with the submittal of the project work plan. Field testing was originally scheduled to begin in August 1980. However, the start of field testing was delayed until May 1981 due to the late delivery of the ash dewatering system (filter presses). The original program included field tests at three power plants. Field testing at the third site was deleted from the test program based on the bench-scale and plant data which indicated a low ash reactivity and no scaling potential for closed-loop operation of this ash system. The testing at Site 1 was approximately 50 percent complete when the project was halted due to insufficient EPA funding for completion of the project. The pilot unit was disassembled and transported to Radian for storage until additional project funding could be provided by EPA.

Additional funding was made available by EPA in August 1982 for continuing the field testing with the ash sluice pilot system at a reduced level of effort. Consequently, sidestream softening was not tested during this program. A fourth power plant, which was not considered in the earlier part of the program, was selected as a host site. This selection was made due to the high reactivity of the fly ash produced and the fact that the plant ash sluice system was operated in a closed-loop mode. This allowed the comparison of pilot results with an operating system. A site visit was made to the plant in August 1982 to solicit the support of the utility and collect a number of water samples from the ash sluicing system and samples of dry ash. Field testing began in October 1982 and was completed in December 1982.

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SECTION 2

SUMMARY OF RESULTS

The primary objective of this project was to investigate the technical feasibility of closed-loop operation of fly ash sluicing systems. To achieve this objective, three major tasks were completed:

- a pilot-scale system to simulate full-scale system operating conditions was designed and constructed,
- field testing with the pilot system was performed to investigate the feasibility of closed-loop mode operation, and
- the ash sluice computer process model was developed and verified using field data.

This section summarizes the results of the field tests using the pilot-scale system. The presentation of these data also includes comparisons with full-scale plant data and predictions of the ash sluice computer process model.

2.1 FIELD TESTING APPROACH

The approach used to evaluate the feasibility of closed-loop operation of an ash sluicing system involved operating the ash sluice pilot system with ash and makeup water from a host power plant. A flow diagram of the ash sluice pilot system is shown in Figure 2-1. The system contains a makeup tank for blending recycled ash sluice water with makeup water. The mixture flows to a mixing tank where fly ash is added to produce a slurry. The mixing tank volume is sufficient to provide a slurry residence time comparable to that required to transport ash from the plant to a settling pond. Additional mixing time can be obtained with the use of the reaction tank. A filter press is

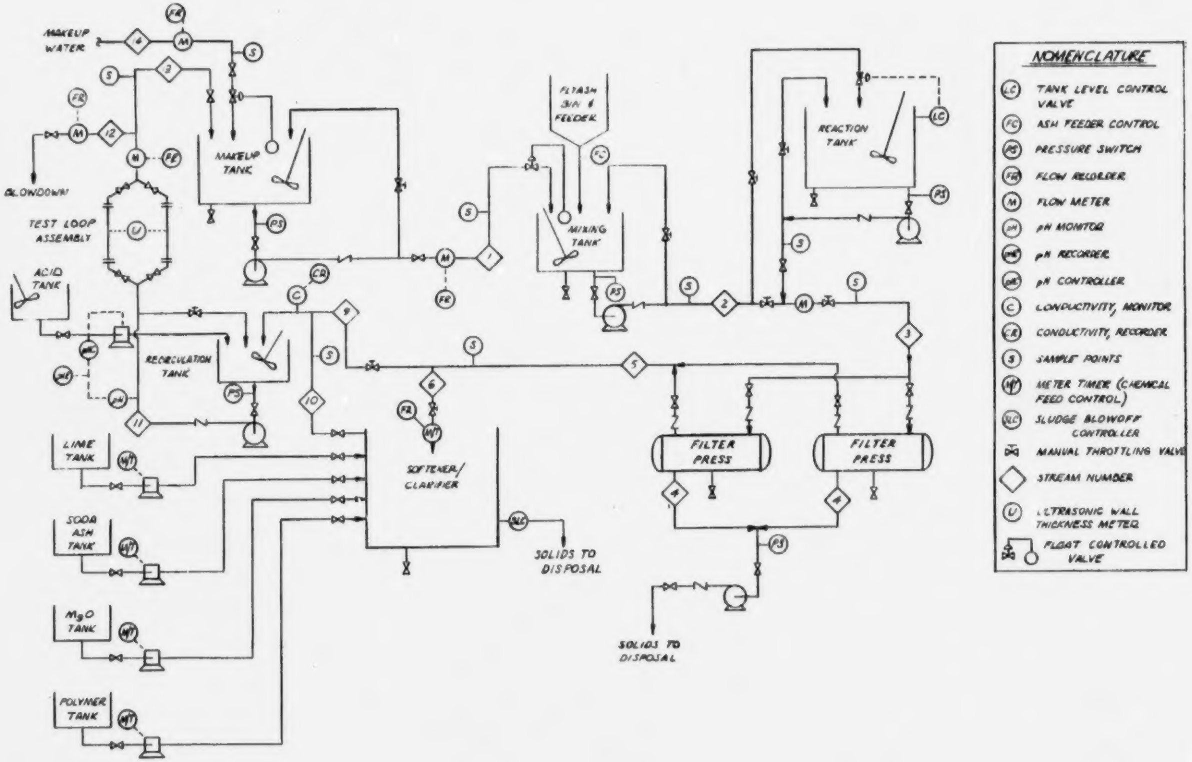

MAKEUP WATER
BLOWDOWN
TEST LOOP ASSEMBLY
ACID TANK
MAKEUP TANK
RECIRCULATION TANK
LIME TANK
SODA ASH TANK
MgO TANK
POLYMER TANK
FLYASH BIN & FEEDER
MIXING TANK
SOFTENER/ CLARIFIER
SOLIDS TO DISPOSAL
REACTION TANK
FILTER PRESS
FILTER PRESS
SOLIDS TO DISPOSAL
NOMENCLATURE
LC TANK LEVEL CONTROL VALVE
FC ASH FEEDER CONTROL
PS PRESSURE SWITCH
FR FLOW RECORDER
M FLOW METER
pH pH MONITOR
pHR pH RECORDER
pHC pH CONTROLLER
C CONDUCTIVITY, MONITOR
CR CONDUCTIVITY, RECORDER
S SAMPLE POINTS
MT METER TIMER (CHEMICAL FEED CONTROL)
SLC SLUDGE BLOWOFF CONTROLLER
MANUAL THROTTLING VALVE
STREAM NUMBER
U ULTRASONIC WALL THICKNESS METER
FLOAT CONTROLLED VALVE

Figure 2-1. Ash Sluice Pilot System Flow Schematic.

used to remove fly ash solids from the system. The filtered water is collected in the recirculation tank and pumped to the makeup tank for reuse. The pilot system includes three treatment options for the control of scaling in the system:

- pH adjustment of the recycle stream,
- sidestream softening of the recycle stream, and
- additional ash slurry mixing time to allow chemical precipitation in a reaction tank.

The system is designed so that one or a combination of these treatment options can be evaluated in a single test run.

Each test run consists of operating the pilot system at a fixed fly ash slurry concentration and blowdown rate. During each test, process flows and ash sluice recycle water chemistry were monitored until steady state chemistry conditions were reached. At this time, a set of samples was collected to characterize each stream in the system. These data were analyzed using the computer process model to determine the scaling tendency of the water. When the pilot unit encountered significant potential for scale formation, additional test runs were conducted using water treatment approaches designed to reduce this scaling tendency. Data from these test runs were used to evaluate the effectiveness of the treatment approach in reducing the scaling tendency of the water and to achieve closed-loop operation.

Pilot testing was conducted at Plant 9677 and Plant 9991 during the program. Both plants produce highly reactive fly ash that results in an alkaline ash sluicing water. The fly ash from Plant 9991 is more reactive than the fly ash from Plant 9677. Plant 9991 burns a low sulfur western subbituminous coal. The fly ash from Plant 9991 contains approximately two times the quantity of leachable calcium as does the fly ash from Plant 9677 which burns a bituminous coal from western Kentucky.

A complete series of tests with and without treatment were planned at each site. However, due to reductions in the project budget, the following tets were performed:

- o Plant 9677
  - no treatment
  - use of a reaction tank to increase contact time;
- o Plant 9991
  - no treatment
  - pH adjustment using sulfuric and hydrochloric acid.

Sidestream softening was not used at either of the plants.

Both plants also sluice ash to settling ponds and reuse pond water for ash sluicing. A portion of the sluice water is discharged from the ash settling pond at Plant 9677. Thus, the ash sluice system is not operated in a closed-loop mode. Some scaling has been observed at this plant. However, since the installation of a pH control system, no scaling has been experienced in any portion of the ash sluicing system at this plant. Plant 9991 operates its ash sluicing system in a closed-loop mode and has experienced some scaling in recirculation pump screens. This scaling has not been severe enough to cause a major plant operating problem. The plant is relatively new and the ash water in the ponds had not experienced a significant increase in dissolved solids at the time of the field tests with the pilot system. Because scaling had been noticed at various points in the system, plant personnel were concerned about scale buildup and scale control. Thus, the pilot system provided an indication of the potential for severe scaling that may occur later in the life of the plant. It also identified potential treatment approaches that may be used to control scaling.

2.2 RESULTS

The major results of the project can be divided into three main areas:

- o ash leaching characteristics,
- o feasibility of closed-loop operation, and
- o verification of the ash sluice computer process model.

A summary of the results in each of these major areas is presented in the remainder of this section.

2.2.1 Ash Leaching Characteristics

During the project the weight fractions of key chemical species leached from fly ash were evaluated based on three sources of data: laboratory leaching tests, pilot unit tests, and full-scale system characterization data. The quantities of species leached from ash during sluicing directly affect the accumulation of dissolved solids in the ash sluice water. High levels of certain species such as calcium, sulfate, and carbonate can result in precipitation and scaling in ash sluice system piping and equipment. Scaling can restrict flow and result in damage due to overheating or poor performance of equipment in the system.

Evaluation of the quantity of ash leached was determined in the laboratory on a batch basis. The water used for the original screening studies for both test sites was deionized water. Measured quantities of ash and deionized water were mixed together until the pH of the solution stabilized. The mixture was then filtered and analyzed for key chemical species (e.g., calcium, magnesium, sodium, potassium, chloride, sulfate, and carbonate). The concentration of each chemical component was then converted into the quantity of that component leached from a measured quantity of ash. In the pilot- and full-scale systems, the chemical characteristics of sluice water before and after sluicing were determined. The net increase in given component was correlated with ash input rate and sluice water flowrate to determine the quantity leached per mass of ash input. During the testing at Plant 9991, this procedure was modified to use ash sluice system makeup water in place of deionized water in order to develop more realistic leaching data.

Table 2-1 summarizes the Plant 9677 ash leaching data from the laboratory batch tests, the full-scale system, and the pilot unit. Both the average and the range of calculated values are reported. Also shown in Table 2-1 are the calcium carbonate and gypsum relative saturation values calculated by the

TABLE 2-1. SUMMARY OF ASH LEACHING DATA--PLANT 9677.

Data Source	Quantity Leached, mg/g ash							Relative Saturation	
	Calcium	Magnesium	Sodium	Potassium	Chloride	Sulfate	Slurry pH	Calcium Carbonate	Gypsum
Field Laboratory[a]									
- average	4.2	0.02	0.12	0.17	0.03	6.5		29	0.3
- range	3.6-5.3	0.01-0.04	0.10-0.16	0.13-0.20	0.00-0.08	4.0-10.1	10.0-11.0	19-45	0.1-0.5
Full-Scale System									
- average	4.1	0.05	0.11	0.25	0.02	6.6		b	0.2
- range	3.2-5.0	0.02-0.07	0.10-0.13	0.22-0.27	0.00-0.03	4.6-8.1	4.7-9.8	0.01-30.8	0.1-0.3
Pilot Unit									
- average	3.3	0.03	0.09	0.18	c	6.5[d]		>100	2.2
- range	2.9-3.8	0.01-0.05	0.02-0.20	0.06-0.35			10.2-10.5		1.9-2.5

[a] Performed using deionized water.

[b] Average not reported due to variations in pH.

[c] No leaching was measured.

[d] Could not be measured due to precipitation of gypsum, and therefore assumed to be the same as the laboratory value.

equilibrium model (as discussed in Section 3) for the leachate composition. The relative saturation values were used to determine if a potential for precipitation existed since any precipitation must be taken into account during the leachability calculations. The relative saturation values indicated that for each of the data sets the potential for precipitation of calcium carbonate existed in the leachate. A potential for gypsum precipitation to affect leaching data existed only for the pilot unit tests.

Based on the average values, the calculated quantitites of species leached for the laboratory and full-scale data agree extremely well. The differences in the relative saturation values presented in Table 2-1 are due primarily to differences in the water (recycled plus makeup) composition prior to being mixed with the ash. The relative saturation values were used to determine if reprecipitation of calcium, sulfate, or carbonate would be expected. The average calculated quantity of calcium leached during pilot testing was approximately 20 percent lower than the average for the laboratory or full-scale data. This does not necessarily indicate a decrease in the quantity of calcium leached, but may reflect additional precipitation of calcium that was not taken into account during the calculation. The transfer of CO_2 from the atmosphere was suspected during the pilot unit test, which could have precipitated with the calcium as calcium carbonate resulting in a lower calculated leach quantity. The quantity of sulfate leaching during the pilot unit tests could not be calculated because of the suspected precipitation of gypsum. For this reason, the laboratory sulfate leaching data were used for pilot unit calculations.

The range values reported in Table 2-1 indicate considerable variation in the calculated leaching quantities. This variation can be attributed to two factors. First, there is some analytical error (±5 percent) associated with the measured values used in the calculation, and second, fluctuations in the coal composition would affect the fly ash composition and the leachability of the species from the fly ash. The comparison of the Plant 9677 leaching data indicates that, although there is a fairly wide range in the values calculated from the three sources, the average values compare well. In addition, the results suggest that for similar ashes the quantities of species leached during pilot- and full-scale sluicing can be adequately estimated from laboratory batch leaching tests. Also, these results suggest that the quantity of a species leached from the ash is not a function of the initial water composition, although at high dissolved solid concentrations reprecipitation of supersaturated species may occur.

Table 2-2 presents the ash leaching data from laboratory, pilot- and full-scale determinations from Plant 9991. The ranges of the quantities of species leached per gram of ash again show considerable overlap between the three data sources. In general, averages of the estimated quantities leached compare reasonably well for all of the species. The most important discrepancy is the estimated quantity of calcium leached from each of the sources, although all of the calcium values are the same order of magnitude. Relative saturation values indicate that calcium carbonate was supersaturated in data obtained from all three data sources. The estimate of the quantity of calcium leached could have been affected if additional CO_2 were absorbed and unaccounted for and leached calcium was precipitated as calcium carbonate during the tests. Since the laboratory apparatus was covered to minimize absorption of CO_2 from the atmosphere, the levels of carbonate were so low that the quantity of calcium carbonate that could have been precipitated would have been minimal. More opportunity for CO_2 transfer and subsequent calcium carbonate precipitation existed in the pilot unit and the greatest opportunity for CO_2 transfer was in the ash ponds of the full-scale system. The greatest uncertainty in the ash leaching data is for the estimates prepared from full-scale data since the weight percent ash in the slurry was not determined. Also, in a full-scale system, CO_2 could be introduced from the following sources:

- as a component of fluidizing air and
- as a component of boiler flue gas contained in the fly ash interstitially or from leaching fly ash hopper valves.

TABLE 2-2. SUMMARY OF ASH LEACHING DATA--PLANT 9991.

	Quantity Leached, mg/g ash							Relative Saturation	
Data Source	Calcium	Magnesium	Sodium	Potassium	Chloride	Sulfate	Slurry pH	Calcium Carbonate	Gypsum
Field Laboratory[a]									
- average	8.1	-	0.37	0.03	0.03	3.7		7.9	0.2
- range	6.2-9.9	-	0.23-0.51	0.0-0.06	0.0-0.06	3.2-4.2	12.2-12.7	7.7-8.1	0.1-0.3
Full-Scale System									
- average	4.0	-	0.43	0.02	0.08	3.0		94	0.3
- range	1.8-7.8	-	0.23-0.78	0.01-0.02	0.08[b]	1.1-7.0	11.1-12.4	65-120	0.2-0.4
Pilot Unit									
- average	5.7	-	0.40	0.05	0.12	2.5		110	0.6
- range	3.5-8.1	-	0.24-0.73	0.04-0.08	0.12[c]	1.9-3.0	11.8-12.6	50-150	0.2-1.3[d]

[a] Performed using plant ash sluice system makeup water.

[b] Based on results from data collected on October 22, 1982.

[c] Based on Test 6 results only.

[d] Gypsum was subsaturated in every test except Test 3.

In summary, the ash leaching data from all three sources are similar, but the laboratory data are considered to be more accurate for use as inputs to the model. Again, differences in the calculated relative saturation values for the three data sets reflect differences in the initial water compositions (prior to ash addition).

2.2.2 Feasibility of Closed-Loop Operation

The primary objective of the program was to evaluate the technical feasibility of operation of an ash sluice system in a closed-loop mode. Pilot unit test results indicated that closed-loop operation would not be possible at either of the plants tested without some form of treatment to control scale formation. Since funding limitations prevented complete test programs using all treatment options from being performed at each plant, the optimum treatment approach and control limits could not be determined. However, two of the three treatment capabilities of the pilot system were used during the two field tests. The results of these test runs are summarized for each plant below.

Table 2-3 summarizes the test conditions and the scaling tendency (relative saturation) of the recycle water for tests at Plant 9677. All tests were conducted with 100 percent recycle of sluice water (closed-loop mode) with slurry concentrations in the 10-12 weight percent range. The only difference between the test runs was the incorporation of more ash mixing time in the reaction/hold tank in Tests 2 and 3. In all tests, the recycle water was supersaturated with respect to both calcium carbonate and gypsum. During the tests, a light coating of scale was noted in several portions of the pilot system. Unfortunately, the program was stopped due to an interruption in funding before enough scale had accumulated for sampling and identification.

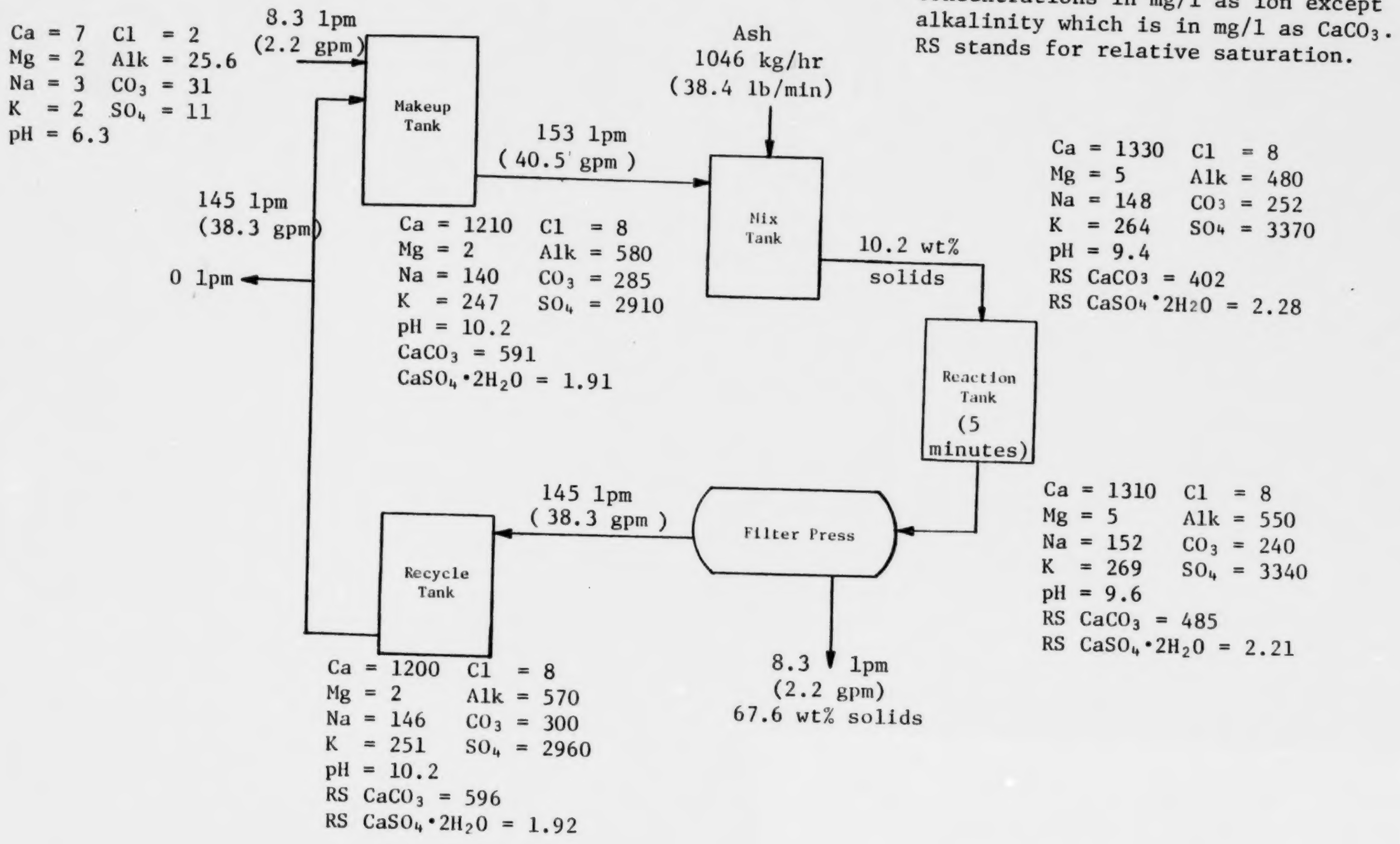
Figure 2-2 presents a chemistry and flow summary for Test 2 at Plant 9677. The calcium carbonate relative saturation is over 400 at all points in the system indicating that precipitation was probably occurring.

TABLE 2-3. SUMMARY OF PILOT TEST RUNS AT PLANT 9677

Test No.	Slurry Concentration wt%	Treatment	Percentage of Sluice Water Recycle	Recycle Water		
				pH	Relative Saturation[a]	
					Calcium Carbonate	Gypsum
1	10.0	_[b]	100	10.5	180	2.5
2	10.2	Reaction tank (5 minute retention)	100	10.2	590	1.9
3	12.8	Reaction tank (10 minute retention)	100	10.4	470	2.1

[a] Relative saturations >1 indicate a potential for precipitation/scale formation.

[b] No treatment.



Concentrations in mg/l as ion except alkalinity which is in mg/l as $CaCO_3$. RS stands for relative saturation.

Ca = 7 Cl = 2
Mg = 2 Alk = 25.6
Na = 3 CO₃ = 31
K = 2 SO₄ = 11
pH = 6.3
8.3 1pm
(2.2 gpm)
Makeup Tank
145 1pm
(38.3 gpm)
0 1pm
153 1pm
(40.5 gpm)
Ca = 1210 Cl = 8
Mg = 2 Alk = 580
Na = 140 CO₃ = 285
K = 247 SO₄ = 2910
pH = 10.2
CaCO₃ = 591
CaSO₄•2H₂O = 1.91
Ash
1046 kg/hr
(38.4 lb/min)
Mix Tank
10.2 wt%
solids
Ca = 1330 Cl = 8
Mg = 5 Alk = 480
Na = 148 CO₃ = 252
K = 264 SO₄ = 3370
pH = 9.4
RS CaCO₃ = 402
RS CaSO₄•2H₂O = 2.28
Reaction Tank
(5 minutes)
Ca = 1310 Cl = 8
Mg = 5 Alk = 550
Na = 152 CO₃ = 240
K = 269 SO₄ = 3340
pH = 9.6
RS CaCO₃ = 485
RS CaSO₄•2H₂O = 2.21
Filter Press
145 1pm
(38.3 gpm)
8.3 1pm
(2.2 gpm)
67.6 wt% solids
Recycle Tank
Ca = 1200 Cl = 8
Mg = 2 Alk = 570
Na = 146 CO₃ = 300
K = 251 SO₄ = 2960
pH = 10.2
RS CaCO₃ = 596
RS CaSO₄•2H₂O = 1.92

Figure 2-2. Summary of Pilot Unit Data from Test 2--Plant 9677.

The gypsum relative saturations also indicate a potential for precipitation. The potential for gypsum precipitation is high because the concentrations of both calcium and sulfate in the recycle water are very high. A significant deposition of gypsum scale may form very rapidly in ash sluice system equipment especially where higher temperatures may be encountered.

The reaction/hold tank was used to provide an additional 5 to 10 minutes of ash mixing time. Bench scale studies had indicated that this approach might be an effective mechanism for increasing precipitation on the ash particles to desupersaturate the sluice water. The results of the field tests at Plant 9677 indicated that only a slight reduction in gypsum relative saturation was obtained. The relative saturation of calcium carbonate increased. Thus, the reaction tank with 5 to 10 minute retention times did not provide a significant reduction in scaling potential. This suggests that longer retention times would be required to promote precipitation (solid/liquid equilibrium) for plants with sluice water compositions similar to Plant 9677 (e.g., plants burning bituminous coals producing alkaline ash sluice water).

Table 2-4 presents a summary of the field tests performed at Plant 9991. Six tests were performed with varying degrees of recycle and slurry concentrations in the 5.8 to 11.9 weight percent range. After baseline tests with no treatment of the recycled ash sluice water, tests were conducted using both sulfuric and hydrochloric acid to control the pH of the recycled water. Due to the higher reactivity of the ash, the approach at Plant 9991 was slightly different from Plant 9677. At Plant 9991 laboratory ash leaching data were input to the ash sluice computer process model, and a blowdown rate was calculated that would maintain gypsum relative saturation at a value of 1.0. Tests 3 through 6 were operated with blowdown and recirculation rates estimated in this manner. A maximum recirculation rate of 78 percent was achieved in Test 4 using hydrochloric acid. The high gypsum relative saturation in Test 3 was the result of a five-fold increase in sulfate concentration in the makeup water. In Tests 5 and 6, higher slurry concentrations were used, and the additional species dissolved in the sluice water at these conditions limited the recycle rate significantly.

TABLE 2-4. SUMMARY OF PILOT TEST RUNS AT PLANT 9991

Test No.	Slurry Concentration wt%	Treatment	Percentage of Sluice Water Recycle	Recycle Water		
				pH	Relative Saturation[a]	
					Calcium Carbonate	Gypsum
1	6.3	–[b]	0	11.9	50	0.2
2	8.8	–[b]	0	12.4	100	0.3
3	5.8	Sulfuric acid[c]	68	9.3	46	1.8[d]
4	5.9	Hydrochloric acid[c]	78	8.4	12	0.6
5	11.9	Hydrochloric acid[c]	56	8.5	12	0.7
6	8.8	Sulfuric acid[c]	27	8.3	6	0.8

[a] Relative saturations >1 indicate a potential for precipitation/scale formation.

[b] No treatment.

[c] pH adjustment with indicated acid.

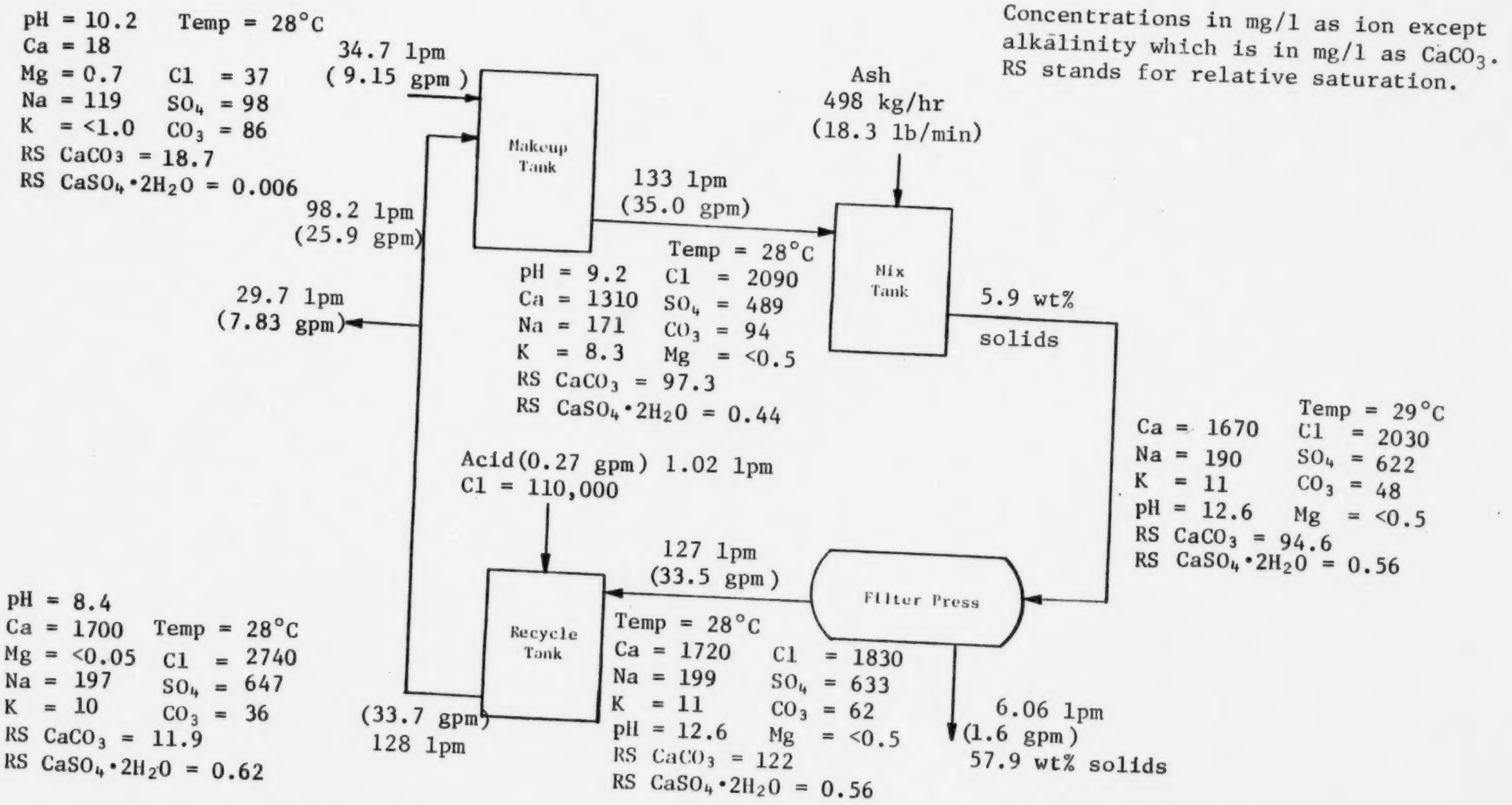
[d] During this test a 5-fold increase in makeup water sulfate concentration occurred.

Figure 2-3 presents a summary of chemistry and flow conditions during Test 4 where hydrochloric acid was used for pH adjustment. The relative saturation of calcium carbonate dropped from 122 to 12 across the recycle tank where the acid is added. Gypsum was subsaturated in this test. However, a further decrease in blowdown would increase the gypsum relative saturation to a critical point. The high calcium and sulfate concentrations in the recycle water indicate that a large quantity of scale may form in the ash sluice system should gypsum become supersaturated.

The test program at Plant 9991 focused on pH adjustment as a means of achieving closed-loop operation without scale formation. Hydrochloric acid was effective in reducing calcium carbonate relative saturation to levels where there was a low potential for precipitation. Sluice water recycle at 78 percent produced a gypsum relative saturation of 0.6 in the recycled sluice water. Sulfuric acid could not be used to control scale in a closed-loop mode sluicing ash from Plant 9991. The sulfate introduced to the pilot unit by sulfuric acid increased the amount of blowdown that was required to avoid gypsum scale formation. At higher slurry concentrations (approximately 10 weight percent) and pH adjustment with hydrochloric acid, recycle rates were limited to approximately 56 percent. pH adjustment with hydrochloric acid can control calcium carbonate scale in a closed-loop mode of operation. However, closed-loop operation may be limited by gypsum scale with this approach.

2.2.3 Verification of Ash Sluice Computer Process Model

A secondary objective of field testing was verification of the capability of the ash sluice computer process model to predict operation of pilot- and full-scale systems. This model was applied in a previous EPA project (EPA Contract No. 68-03-2339) and has been used to predict the potential for scaling under various ash loading and water quality conditions. Since the model was developed, its capability had not been verified with actual field data. The ash sluice pilot project provided an excellent opportunity for verifying and improving the model. The model was used to evaluate plant data collected during site visits. These evaluations served as a basis for developing the test plans at each site.


pH = 10.2 Temp = 28°C
Ca = 18
Mg = 0.7 Cl = 37
Na = 119 SO₄ = 98
K = <1.0 CO₃ = 86
RS CaCO₃ = 18.7
RS CaSO₄•2H₂O = 0.006
34.7 lpm
(9.15 gpm)
Makeup Tank
98.2 lpm
(25.9 gpm)
29.7 lpm
(7.83 gpm)
133 lpm
(35.0 gpm)
Temp = 28°C
pH = 9.2 Cl = 2090
Ca = 1310 SO₄ = 489
Na = 171 CO₃ = 94
K = 8.3 Mg = <0.5
RS CaCO₃ = 97.3
RS CaSO₄•2H₂O = 0.44
Ash
498 kg/hr
(18.3 lb/min)
Mix Tank
5.9 wt%
solids
Temp = 29°C
Ca = 1670 Cl = 2030
Na = 190 SO₄ = 622
K = 11 CO₃ = 48
pH = 12.6 Mg = <0.5
RS CaCO₃ = 94.6
RS CaSO₄•2H₂O = 0.56
Acid(0.27 gpm) 1.02 lpm
Cl = 110,000
127 lpm
(33.5 gpm)
Filter Press
Recycle Tank
pH = 8.4
Ca = 1700 Temp = 28°C
Mg = <0.05 Cl = 2740
Na = 197 SO₄ = 647
K = 10 CO₃ = 36
RS CaCO₃ = 11.9
RS CaSO₄•2H₂O = 0.62
(33.7 gpm)
128 lpm
Temp = 28°C
Ca = 1720 Cl = 1830
Na = 199 SO₄ = 633
K = 11 CO₃ = 62
pH = 12.6 Mg = <0.5
RS CaCO₃ = 122
RS CaSO₄•2H₂O = 0.56
6.06 lpm
(1.6 gpm)
57.9 wt% solids

Concentrations in mg/l as ion except alkalinity which is in mg/l as $CaCO_3$. RS stands for relative saturation.

Figure 2-3. Summary of Pilot Unit Data from Test 4--Plant 9991.

]

The model consists of an internal chemical equilibrium model supported by a set of subroutines. The equilibrium model calculates ionic interactions and the potential for precipitation of solids in aqueous systems which contain the following species:

- calcium
- magnesium
- sodium
- potassium
- ammonia
- silica
- chloride
- carbonate
- nitrate
- sulfate
- phosphate

The support subroutines simulate the various components of an ash sluicing system (pond, softener, reaction/hold tank, etc.) and perform material balance calculations.

As discussed in Section 2.2.2, the model was used to predict the blowdown flowrates that would result in a gypsum relative saturation value of 1.0 in the recycled sluice water for Plant 9991. For Tests 4 through 6 at Plant 9991 in Table 2-4, the gypsum relative saturations ranged from 0.6 to 0.8 based on measured blowdown compositions. One set of chemistry and ash leaching data were used to predict blowdown flowrates for the tests. In the field, these chemistries and ash leaching rates varied during the test run resulting in the differences shown.

The output of the model can only be as accurate as the quality of the input data to the model. If the input data (e.g., ash leaching, makeup water chemistry) accurately reflect the characteristics of an ash sluice system, then the model predictions should predict system chemistry and flows relatively accurately. Table 2-5 presents a comparison of the chemistry, relative saturation, and system flowrates measured during Test 4 in the pilot system and predicted by the model. Ash leach rates, makeup water composition, and the approach to solid-liquid equilibrium measured in the pilot system were used as inputs to the model. The model accurately predicted all chemistry and

TABLE 2-5. COMPARISON OF ASH SLUICE MODEL PREDICTIONS WITH PILOT UNIT PERFORMANCE FOR TEST 4

	Predicted by Model	Measured in Pilot Unit	Difference (Percent)
System Blowdown Composition			
Component, ppm as ion			
Ca	1650	1700	3
Mg	0.2	<0.5	N/A[a]
Na	186	197	6
K	9.6	10	4
Cl	2670	2740	3
Alkalinity (as $CaCO_3$)	14.8	30	50
SO_4	722	647	-12
pH	8.4[b]	8.4	0
Relative Saturation			
$CaCO_3$	4.8	11.9[c]	150
Gypsum	0.68	0.62[c]	-9
System Flow Rates, lpm (gpm)			
Hydrochloric acid	0.796 (0.21)	1.02 (0.27)	22
Makeup	33.7 (8.9)	34.9 (9.2)	3
Sludge (water loss)	5.68 (1.5)	6.06 (1.6)	6

[a] N/A - Not Applicable.

[b] The pH was specified as a model input and the resulting acid addition rate was calculated.

[c] Calculated by the model based on measured compositions of pilot plant blowdown.

flow rate data within the limits of analytical and flow measurement accuracy (±20 percent). The only significant deviation is in the prediction of alkalinity which directly affects the relative saturation calculations. Although the relative error of the alkalinity is high, the actual concentrations involved are fairly low. Thus, even though the driving force for scaling (relative saturation) is high, the quantity of material that could potentially be deposited is relatively small.

In order to demonstrate the predictive capability of the model, data from Test 4 was used to project the minimum blowdown that could be achieved without gypsum supersaturation. Hydrochloric acid was used to adjust the pH of recycle water in this test. The blowdown composition for the minimum blowdown case is compared with the model prediction for Test 4 (78 percent recycle) in Table 2-6. At a 94 percent sluice water recycle rate, gypsum would become supersaturated indicating that closed-loop operation may result in precipitation. This prediction was not verified due to the abbreviated field program; however, from the previous discussion showing the accurate duplication of field test results, this estimate should be reasonably accurate. Although gypsum scale formation had not been encountered at Plant 9991, the concentrations of species in the full-scale system were much lower than predicted by the model. This indicates that the plant has not yet reached steady-state operation. Due to the large volumes of the ash ponds and the firing rate at the plant, several years could be required before gypsum scaling is observed.

The ash sluice computer process model was successfully used to specify test conditions. The predicted results correlate well with measured operating conditions. The model's predictive capabilities are limited, however, by the difficulty in obtaining representative data for use as inputs (ash reactivity, CO_2 transfer, etc.). The model is an effective tool in evaluating the relative effects on the operation of a recirculating ash sluicing system caused by variations of certain parameters (e.g., slurry concentration, pH, ash leaching characteristics, closed loop operation).

TABLE 2-6. COMPARISON OF MINIMUM BLOWDOWN SIMULATION WITH SIMULATION OF TEST 4.

	Model Predicted Minimum Blowdown	Pilot Unit Test 4
System Blowdown Composition		
Component, ppm as ion		
Ca	3910	1650
Mg	0.1	0.2
Na	343	186
K	23.8	9.6
Cl	6695	2670
Alkalinity (as $CaCO_3$)	7.5	14.8
SO_4	1036	722
pH	8.4[a]	8.4
Relative Saturation		
$CaCO_3$	3.1	4.8[b]
Gypsum	1.1	0.68[b]
System Flow Rates, lpm (gpm)		
Hydrochloric Acid	0.796 (0.21)	0.796 (0.21)
Makeup	12.5 (3.3)	33.7 (8.9)
Sludge (water loss)	5.68 (1.5)	5.68 (1.5)
Liquid Blowdown	7.58 (2.0)	28.8 (7.6)
Total Blowdown	13.3 (3.5)	34.5 (9.1)

[a] The pH was specified as a model input and the resulting acid addition rate was calculated.

[b] Calculated by the model based on measured compositions of pilot plant blowdown.

2.3 CONCLUSIONS

The technical feasibility of achieving closed-loop operation of a fly ash sluice system was investigated at Plant 9677 and Plant 9991. The evaluation was based on 1) data obtained from a characterization of the full-scale systems, 2) pilot unit testing at each plant, and 3) ash sluice process model simulations. Based on the results of the program, the following conclusions were reached:

- Closed-loop operation of fly ash sluicing systems handling highly reactive alkaline ashes (characteristic of low sulfur western coal ashes) can not be achieved without encountering precipitation in the system unless water treatment techniques are employed to control scale formation. The results obtained from the full-scale plant characterization, pilot unit, and ash sluice computer model are consistent in indicating precipitation will occur. While precipitation in the sluicing line has been observed in spite of the erosive or scouring nature of the ash, scale formation in the return water and distribution lines may be even more of a problem and increase pressure drop and reduce flow rates to the point where maintenance is required to provide adequate system reliability.

- Acid addition for pH adjustment should be effective in controlling calcium carbonate scale formation in the sluice water return line. Economic considerations will probably favor sulfuric acid use over hydrochloric acid; however, use of sulfuric acid will increase the potential for gypsum scale formation. Gypsum scale is perceived to be less desirable than calcium carbonate scale. Ash pond water blowdown must be sufficient to prevent gypsum scale. Therefore, gypsum was ultimately the limiting species which prevented reliable closed-loop operation at the plants tested. Increased ash/water contact time in a reaction tank was not adequate to control the potential for gypsum scale formation at the residence times tested (5 to 10 minutes). Other treatment techniques, such as sidestream softening, will be necessary to prevent gypsum scale formation during closed-loop operation.

- The ash sluice computer model was verified as an effective tool for predicting the chemical composition and potential for scale formation in the pilot unit when accurate inputs to the model were specified. Critical inputs to the model that can significantly affect the accuracy of model predictions include 1) ash leaching data, 2) the quantity of CO_2 transfer in the ash ponds, and 3) estimates of the potential for precipitation in ash sluice equipment. Results of the program indicate that laboratory ash leaching data are adequate to use as inputs to the model. CO_2 transfer was minimized by the pilot unit design, but the long residence times in the full-scale system ponds could result in the transfer of CO_2. However, full-scale plant data indicate that equilibrium is not reached between CO_2 in the pond water and the atmosphere indicating that CO_2 transfer is fairly minimal. Pilot unit data indicated that less than 50 percent of the supersaturated species are precipitated in sluicing equipment. More accurate estimates of CO_2 transfer and approach to solid/liquid equilibrium would enable more accurate model predictions to be provided.

2.4 RECOMMENDATIONS

The usefulness of the pilot unit data and ash sluice computer model in evaluating the feasibility of closed-loop operation was demonstrated in the program. Several factors were identified which limited the ability to achieve or operate ash sluicing systems reliably in a closed-loop mode. Limitations in the ability of the computer model to more accurately predict full-scale system operation were also identified. The following recommendations are proposed to address the limitations encountered in the program:

- Additional pilot unit testing and full-scale characterization data should be collected at power plants firing coals with different ash characteristics to 1) broaden the available data base, 2) evaluate the feasibility of closed-loop fly ash sluicing at other plants, and 3) provide longer-term runs to verify computer model predictions. Data were collected in this study at plants firing coals producing highly alkaline ashes with a large fraction of soluble calcium. However, laboratory data collected in earlier projects indicated that closed-loop operation may be more feasible at plants handling less reactive ashes.

- The feasibility of closed-loop operation for bottom ash sluice systems should be investigated. Bottom ash is frequently sluiced in common ash handling systems with fly ash and can, therefore, affect the feasibility of closed-loop operation for the overall system. Alternatively, bottom ash is often sluiced alone when fly ash is handled by dry transport methods. Closed-loop bottom ash sluice system operation may be required by local regulations or can be necessary in some regions of the country where water availability is a primary concern.

- Additional water treatment techniques to control scale formation should be investigated to allow systems to operate reliably in the closed-loop mode. In particular, water treatment approaches which are effective in controlling gypsum scale formation should be investigated. One or more water softening approaches to reduce calcium hardness are recommended for evaluation. The treatment approaches should be selected for testing and piloting before being suggested for use in a full-scale plant based on their particular applicability to ash sluice systems and the cost/benefits of the treatment techniques.

- Additional data should be collected to allow users of the ash sluice model to specify accurate inputs for the model. A larger ash leaching data base and/or improved laboratory ash leaching procedures would be useful. Also, additional data on the extent of CO_2 transfer in ash ponds and precipitation in the sluicing equipment are necessary. Once the ability of the ash sluice model to predict the performance of full-scale systems has been improved, this capability should be used to achieve closed-loop operation at a operating power plant or in the design of a new facility.

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SECTION 3

USER'S MANUAL FOR THE ASH SLUICE SYSTEM COMPUTER MODEL

3.1 INTRODUCTION

An objective of the pilot test program was to evaluate the ability of the ash sluice system computer model to simulate a recirculating ash sluice system. This evaluation affected the approach used during pilot testing. Therefore, an understanding of the model's capabilities and limitations is necessary to provide a background before the results of the field test program are presented.

The ash sluice system computer model was developed as a tool to determine the influence of different process parameters and treatment options on the chemistry of a recirculating ash sluice water system. The model can be used both as an aid in the design of new systems and to study the effect of proposed changes on an existing system. It should be noted that the ash sluice system computer model is a steady-state model. Stream compositions and flow rates calculated by the model are for the system at steady state. The time required to reach steady state is not considered by the model.

Based on input information, the model calculates the potential for solids formation in the major ash sluice system streams. If required, the user may then change process variables (such as makeup water quality, weight percent ash in sluice line, or blowdown flow rate) or consider different treatment options (such as acid addition, reaction/hold tank or sidestream softening) to reduce the potential for solids formation to an acceptable level.

In this section, a description of the ash sluice system computer model is provided, followed by instructions for its use. Four example cases are presented and discussed.

3.2 DESCRIPTION OF THE COMPUTER MODEL

The ash sluice system computer model was developed to simulate a recirculating ash sluice water system. The purpose of the model is to provide the user with the information needed to determine the requirements for scale-free operation of a system without actual field testing. A complete listing of the program and subroutines is provided in Appendix D.

3.2.1 Basic Model Design

The ash sluice model consists of an internal chemical equilibrium model supported by a set of subroutines which simulate various equipment items in an ash sluice system. The equilibrium model calculates ionic interactions and the potential for solids formation in aqueous systems which contain the following species:

- calcium
- magnesium
- sodium
- potassium
- ammonia
- silica
- chloride
- carbonate
- nitrate
- sulfate
- phosphate

The equilibrium model data base contains the information needed to calculate equilibrium constants and species activities for the various chemical reactions. A complete set of the reactions considered by the equilibrium model is presented in Appendix A. Equilibrium constants are calculated as a function of temperature according to the following equation:

$$\log_{10}K = A_1T^{-1} - A_2\log_{10}T - A_3T + A_4 \qquad (3\text{-}1)$$

where:

K = equilibrium constant (moles solute/kg H_2O),
T = temperature (°K), and
A_1 to A_4 = constants for each reaction.

Activities for the various chemical species are calculated using the following equation:

$$a_i = \gamma_i m_i \qquad (3\text{-}2)$$

where:
a_i = activity of chemical species i (g-moles/kg H_2O),
γ_i = activity coefficient of chemical species i, and
m_i = molality of chemical species i (g-mole/kg H_2O).

The activity coefficients are calculated using a correlation developed by Bromley (3).

Based on the values calculated, the potential for precipitation of solid species is determined. This is accomplished by calculating the relative saturation (RS) values for the possible solid species. The relative saturation is a measure of the driving force for the precipitation of a solid. For example, the relative saturation of calcium carbonate is defined as:

$$RS(CaCO_3) = \frac{a(Ca^{++})\ a(CO_3^{=})}{K_{sp}\ (CaCO_3)} \qquad (3\text{-}3)$$

where:
$RS(CaCO_3)$ = the relative saturation of calcium carbonate,
a = the activity of either calcium (Ca^{++}) or carbonate ($CO_3^{=}$), and

K_{sp} = the solubility product of calcium carbonate ($CaCO_3$).

For a relative saturation of 1.0, the system is at solid/liquid equilibrium with respect to that species. If the relative saturation is less than 1.0, the system is subsaturated. And, if the relative saturation is greater than 1.0, the system is supersaturated and potential for solids formation exists.

The subroutines supporting the equilibrium model can be divided into the following four categories:

- executive subroutines,
- equipment subroutines,
- service subroutines, and
- convergence subroutines.

A list of the subroutines and their functions is presented in Table 3-1. FORTRAN code for each subroutine is included in Appendix D.

The executive subroutines read and transfer all input information, determine the ash sluice system configuration, set the order of calculations, and execute the simulation by calling the different subroutines in the appropriate order.

The equipment subroutines simulate specific process operations within the ash sluice water system. Although these operations are typically associated with equipment items (such as a reaction tank or softener), equipment subroutines also simulate process stream dividers (tees) and addition points, initiate the inlet stream compositions for ash and makeup water to the system (based on user input values), and perform overall mass balance calculations to check for conservation of species.

Service subroutines support equipment subroutines by performing routine calculations such as calculating the total mass flow rate of various streams, summing the total amounts of each species, and checking material balances. All subroutines providing printout are considered service subroutines.

TABLE 3-1. ASH SLUICE SYSTEM COMPUTER MODEL SUMMARY OF SUBROUTINES

Subroutine Type	Subroutine Name	Function of Subroutine
EXECUTIVE	XEX001	Calls major executive and printout routines.
	XEX002	Reads input data, builds process matrix based on user options, and determines the order of calculations.
	XEX003	Calls equipment routines to echo print input data.
	XEX004	Calls equipment routines according to the order of calculations to perform the various equipment calculations.
	XEX005	Matches equipment name with identifying number.
	XEX006	Used by XEX003 and XEX004 to call the appropriate equipment routines.
EQUIPMENT	XEQ001	Calculates initial guesses for makeup flow rate, acid addition rate, sidestream treatment rate and blowdown composition and performs material balance calculations around the whole system.
	XEQ002	Initializes ash stream.
	XEQ003	Initializes chemical addition stream for either acid addition or sidestream softening.
	XEQ004	Initializes makeup water stream.
	XEQ005	Simulates CO_2 transfer and precipitation of solids in the pond.
	XEQ006	Simulates solids precipitation occurring in a reaction/hold tank due to increased ash/water contact time.
	XEQ007	Simulates single stage lime/soda sidestream softener.
	XEQ008	Combines a minimum of two and a maximum of four streams into one stream.
	XEQ009	Divides one stream into two streams.
	XEQ010	Initiates wastewater stream.
SERVICE	XSE001	Sums the species for a minimum of two and a maximum of four stream vectors.
	XSE002	Prints summary table after each iteration.
	XSE003	Performs a material balance for the equipment subroutines.
	XSE004	Performs all necessary unit conversions for the detailed stream information tables printed at the conclusion of each simulation.
	XSE005	Calculates the total molar rate of each atomic species for a particular stream.
	XSE006	Prints all information stored in a stream vector array.
	XSE007	Prints detailed stream information tables at the conclusion of each simulation.
	XSE008	Determines the total amount of key species in the liquid phase or the solid phase or both, and stores them in the appropriate stream vector locations.
	XSE009	Calculates the mass rate of all or part of a given stream vector.
CONVERGENCE	XCO001	Converges on the user specified recirculating water alkalinity.
	XCO002	Converges on the user specified recirculating water pH.
	XCO003	Converges on the user specified calcium carbonate relative saturation.
	XCO004	Checks the difference in the blowdown composition for the previous and current iterations and keeps track of the number of iterations completed.

Two types of convergence subroutines are used in the ash sluice model. The first type adjusts the amount of a given chemical species in order to converge on a user specified stream parameter such as pH, alkalinity or relative saturation. The second type is used to check for overall system convergence following a sequence of iterative calculations for the recirculating ash sluice water loop.

The transfer of information among the subroutines is accomplished through a data storage matrix which is common to both the equilibrium model and the support subroutines. The data matrix is structured to store stream specific information for each process stream in the system. Each row of the matrix is referred to as a stream vector. A complete listing of the information stored in a stream vector (S.V.) is presented in Table 3-2.

3.2.2 Capabilities and Limitations

The two most common types of scale formation found in ash sluice systems are calcium carbonate and gypsum. These are the major solid species considered by the model. For a given system, the user has several options if the computer model indicates that a potential for solids formation exists (when the calculated relative saturation value for any potential scaling species is greater than 1.0). First, the user can adjust various process parameters to reduce the quantity of dissolved solids in the system. This would include the use of a higher quality makeup water or an increase in the blowdown flow rate. If satisfactory results are not obtained, the user may consider employing some type of water treatment.

A potential for precipitation of a compound exists theoretically any time the relative saturation of that species exceeds 1.0. However, in actual systems rapid scaling may not occur until a higher relative saturation is reached. Experience with gypsum indicates that at a relative saturation of less than 1.3, scaling will probably not occur. Calcium carbonate scaling is not normally expected until a relative saturation of 2.5 is exceeded. An exception to these maximum relative saturation values occurs when one component (either cationic or anionic) of the compound is present in very low

TABLE 3-2.

DEFINITION OF STREAM VECTOR LOCATIONS

S.V. Location	Parameter	Units
1-4	Flags	
5	Temperature	°K
6	Pressure	atm
7	Enthalpy	cal/sec
8-9	blank	
10	Total gas	g-mole/sec
11	N_2 (gas)	g-mole/sec
12	O_2 (gas)	g-mole/sec
13	H_2O (gas)	g-mole/sec
14	CO_2 (gas)	g-mole/sec
15-18	blank	
19	$P^*_{CO_2}$	atm
20	Total Ca	g-mole/sec
21	Total Mg	g-mole/sec
22	Total Na	g-mole/sec
23	Total NH_3	g-mole/sec
24	Total K	g-mole/sec
25	Total Cl	g-mole/sec
26	Total CO_2	g-mole/sec
27	Total NO_3	g-mole/sec
28	Total SO_4	g-mole/sec
29	Total SiO_2	g-mole/sec
30	Total PO_4	g-mole/sec
31	Total H_2O	g-mole/sec
32	Total Inerts	g-mole/sec
33-37	blank	
38	TDS	ppm
39	Ionic strength	
40	pH	
41	H_2O (liq)	g/sec
42	H^+	g-mole/kg H_2O
43	OH^-	g-mole/kg H_2O
44	H_2CO_3(liq)	g-mole/kg H_2O
45	HCO_3^-	g-mole/kg H_2O
46	HNO_3^-	g-mole/kg H_2O
47	$H_2SiO_4^{=}$	g-mole/kg H_2O
48	HSO_4^-	g-mole/kg H_2O
49	$H_3SiO_4^-$	g-mole/kg H_2O
50	$CaOH^+$	g-mole/kg H_2O
51	$CaHCO_3^+$	g-mole/kg H_2O
52	$CaCO_3$(liq)	g-mole/kg H_2O
53	$CaNO_3^+$	g-mole/kg H_2O
54	$CaSO_4$(liq)	g-mole/kg H_2O
55	$MgOH^+$	g-mole/kg H_2O
56	$MgHCO_3$	g-mole/kg H_2O
57	$MgCO_3$(liq)	g-mole/kg H_2O
58	$MgSO_4$(liq)	g-mole/kg H_2O
59	NaOH(liq)	g-mole/kg H_2O
60	$NaHCO_3$(liq)	g-mole/kg H_2O
61	$NaCO_3^-$	g-mole/kg H_2O
62	$NaNO_3$(liq)	g-mole/kg H_2O
63	$NaSO_4^-$	g-mole/kg H_2O
64	NH_3(liq)	g-mole/kg H_2O
65	$NH_4SO_4^-$	g-mole/kg H_2O
66	NH_4HSO_4(liq)	g-mole/kg H_2O
67	$NH_4CO_3^+$	g-mole/kg H_2O
68	NH_4HCO_3(liq)	g-mole/kg H_2O
69	H_3PO_4(liq)	g-mole/kg H_2O
70	$H_2PO_4^-$	g-mole/kg H_2O
71	$HPO_4^{=}$	g-mole/kg H_2O
72	$CaH_2PO_4^+$	g-mole/kg H_2O
73	$CaHPO_4$(liq)	g-mole/kg H_2O
74	$CaPO_4^-$	g-mole/kg H_2O
75	$MgHPO_4$(liq)	g-mole/kg H_2O
76	NH_2COO^-	g-mole/kg H_2O
77	KSO_4^-	g-mole/kg H_2O
78	Ca^{++}	g-mole/kg H_2O
79	Mg^{++}	g-mole/kg H_2O
80	Na^+	g-mole/kg H_2O
81	NH_4^+	g-mole/kg H_2O
82	K^+	g-mole/kg H_2O
83	Cl^-	g-mole/kg H_2O
84	$CO_3^{=}$	g-mole/kg H_2O
85	NO_3^-	g-mole/kg H_2O
86	$SO_4^{=}$	g-mole/kg H_2O
87	H_4SiO_4(liq)	g-mole/kg H_2O
88	$PO_4^{=}$	g-mole/kg H_2O
89-99	blank	
100	RS of $CaSO_4 \cdot 2H_2O$	
101	RS of $CaCO_3$	
102	RS of $Mg(OH)_2$	
103-104	blank	
105	Wt frac susp sol	
106	$Ca(OH)_2$(sol)	g-mole/sec
107	$CaCO_3$(sol)	g-mole/sec
108	$Ca_3(PO_4)_2$(sol)	g-mole/sec
109	$CaSO_4$(sol)	g-mole/sec
110	$CaSO_4 \cdot 2H_2O$ (sol)	g-mole/sec
111	$Mg(OH)_2$(sol)	g-mole/sec
112	$MgCO_3 \cdot 5H_2O$ (sol)	g-mole/sec
113	Sepiolite (sol)	g-mole/sec
114	CaH_2SiO_4(sol)	g-mole/sec
115	SiO_2(sol)	g-mole/sec
116	$CaHPO_4$(sol)	g-mole/sec
117	Na_2CO_3(sol)	g-mole/sec
118	Inerts	g-mole/sec
119-130	blank	

concentration and the other in high concentration. In this case there may be a high relative saturation (strong driving force for scaling), but the low concentration of one component limits the amount of scale deposition that can occur. For example, the effluent from a lime/soda ash softener typically has a very low concentration of calcium (~14 mg/l) and a large excess of carbonate alkalinity. At the pH (>10) normally encountered, the relative saturation with respect to calcium carbonate generally falls in the range of 15 to 20. This indicates a strong scaling potential; however, the calcium level is so low that little, if any, scaling would occur.

If the relative saturation value for calcium carbonate in the recirculating water is greater than 1.0 (or the limit desired by the user), acid addition for pH reduction may be considered to reduce the potential for calcium carbonate scale formation. However, acid addition is not a viable method of reducing gypsum scale potential since reduction of pH alone does not significantly affect the relative saturation of gypum. Incorporation of a reaction/hold tank into the ash sluice system can also be considered to provide additional ash/sluice water mixing time. An additional treatment option would be to soften a slipstream of the recirculating water. This would remove a portion of the calcium from the recirculating water and reduce the scaling potential for both calcium carbonate and gypsum.

A limitation of the ash sluice system model, like any other computer model, is the fact that the accuracy of the simulation results reflect the accuracy of the input data. Several variables can significantly affect the recirculating ash sluice water composition (and therefore the calculated potential for scale formation). However, data are not available to allow the model to accurately predict the influence of several important variables on sluice water chemistry. Therefore, the user must specify these variables as inputs to the model. These include:

- the quantity of soluble species leached from the ash,
- the CO_2 transfer between the pond water and the atmosphere, and
- the degree of solids precipitation occurring in the pond.

These variables are discussed in more detail below.

3.2.2.1 Ash Leaching--

In cases where makeup water available to the ash sluice system is relatively low in dissolved solids, the soluble species contributed by the ash are considerably greater in the sluice water than the species contributed by the makeup water. For such systems, the makeup water quality does not significantly influence the recirculating water composition. Therefore, the ability to accurately simulate the ash sluice system chemistry is highly dependent upon the accuracy of the leaching data used as input for the model.

The quantity of species leaching from the ash may be influenced by the type of coal being burned, the boiler configuration, the type of ash being sluiced (bottom, economizer, or fly) and the contact time of the ash and water. However, adequate data are not available at this time to estimate the quantity of material leaching from the ash based on these factors. For this reason, a laboratory leaching test procedure was developed. The test procedure involves mixing an ash sample (either an actual sample from an operating system or a sample from a plant burning a similar coal for a system being designed) with deionized water for approximately 30 minutes. By analyzing the resulting liquor, the quantity leaching from the ash can be calculated. A more detailed description of the laboratory procedure is presented in Section 4.0. This information is used as input to the model; however, the laboratory test may not adequately account for factors affecting actual leaching in the ash sluice system such as contact time and sluice water composition (if actual sluice water samples are not available).

3.2.2.2 Carbon Dioxide Transfer--

Carbon dioxide (CO_2) transfer occurs in the ash pond due to a difference in the partial pressure of CO_2 in the atmosphere and the partial pressure of CO_2 in the sluice water. Depending upon the quantity of CO_2 in the system and the pH of the pond water, a driving force for either absorption or desorption of CO_2 may exist in the pond. While the actual amount of CO_2 transferring is influenced by the driving force, it may also be influenced by the mixing in the pond due to wind and the pond residence time. For modeling purposes, the actual operating conditions can be bounded by simulating two cases. The first case is to simulate the system by assuming that no CO_2 transfer occurs between the pond and the atmosphere. Alternatively, the second case can be simulated by assuming that the pond reaches gas/liquid equilibrium with respect to CO_2 in the atmosphere. However, based on the data from several full-scale systems, very little CO_2 transfer occurs in the pond and thus gas/liquid equilibrium with CO_2 in the atmosphere is not reached. Adequate data are not currently available to reliably predict the quantity of CO_2 that transfers.

By using the model and assuming that no CO_2 transfer occurs, an approximation of conditions that would normally be expected in a pond can be predicted. Additional modeling using various approaches to equilibrium provide the user with a method of evaluating the sensitivity of the scaling potential of the water as a function of CO_2 transfer. Where a high sensitivity is indicated, additional field testing to determine approach to CO_2 equilibrium with the atmosphere may be required.

3.2.2.3 Precipitation of Solids in the Pond—

The third factor influencing the simulation results is the quantity of solids precipitating in the pond. From past experience, it is known that some precipitation of solids occurs in an ash pond. It is also known that for some systems, the pond water does not achieve solid-liquid equilibrium since calcium carbonate and gypsum relative saturation values greater than 1.0 have been calculated for the recirculating water. The modeling approach typically used with respect to the precipitation of solids in the pond is to first assume no solids formation occurs and then to assume solid-liquid equilibrium in the pond is achieved.

For an operating system, the approach to equilibrium, App_{eq}, can be calculated by the following equation:

$$App_{eq} = \frac{Ca_{max} - Ca_{meas}}{Ca_{max} - Ca_{min}} \qquad (3-4)$$

where:

Ca_{max} = the calcium calculated from the leaching information assuming no precipitation,

Ca_{meas} = the measured calcium in the pond water, and

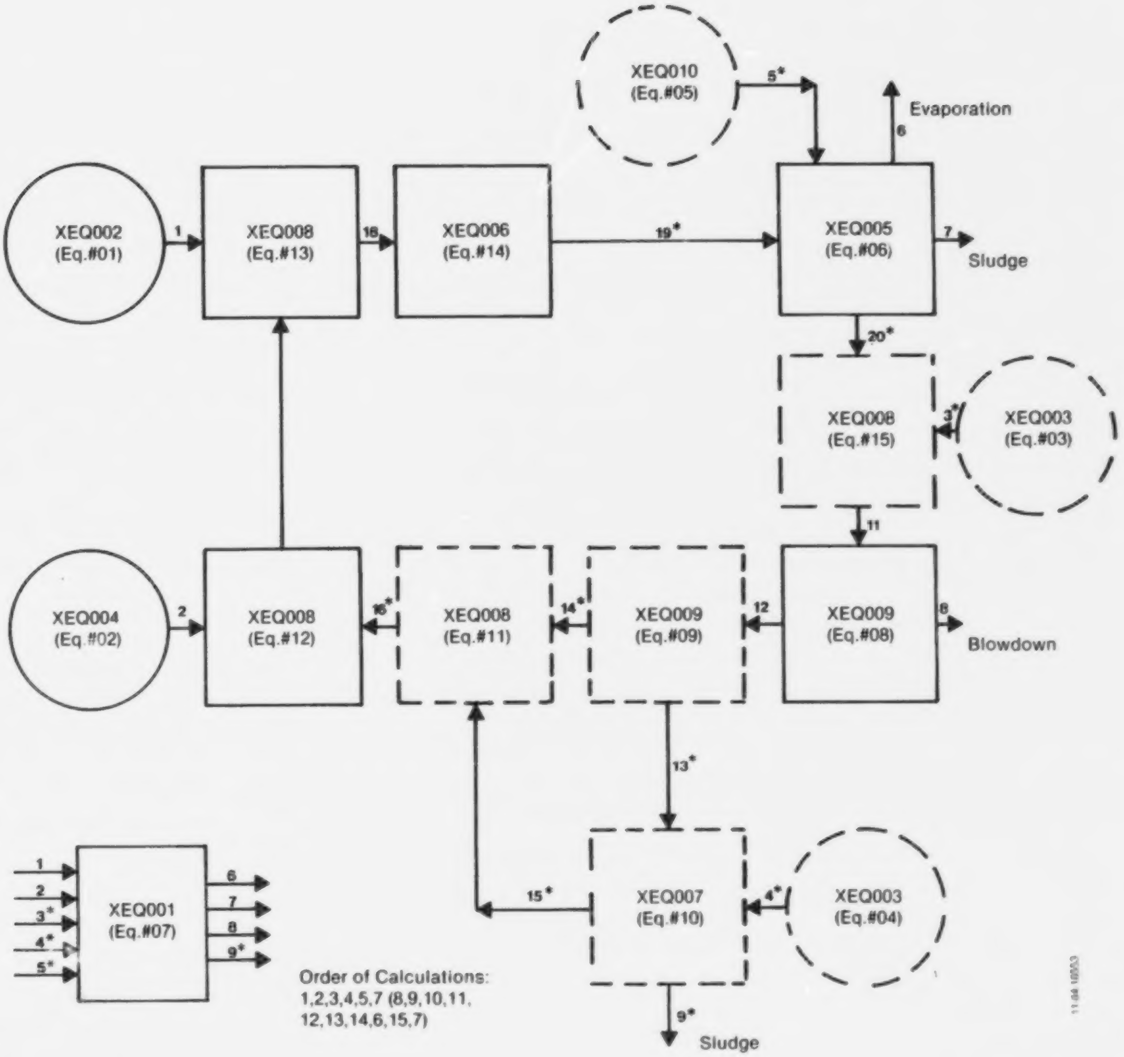
Ca_{min} = is the calcium concentration assuming the system is at solid-liquid equilibrium.

Based on data from pilot test and full-scale systems, a reasonable value for the approach to solid-liquid equilibrium in the pond to use in the design of new systems would be 0.40 to 0.60.

3.2.3 Ash Sluice System Configuration

The system configurations simulated by the model are illustrated in Figure 3-1. Each square or circle represents an equipment subroutine called during the simulation. Those shown in dashed lines are called only if that particular treatment or process option is specified by the user. The stream numbers marked with an asterisk are not used during the simulation unless the adjacent optional subroutines are called. For example, if the user did not specify the reaction tank option (subroutine XEQ006), stream 18 (not 19) would represent the stream from XEQ008 (equipment number 13) to the pond (equipment number 06).

The order of calculations shown in Figure 3-1 is the logic used by the program to perform the simulation. The numbers listed are the equipment numbers for the various equipment subroutines. Each subroutine is called in the order shown. Subroutines represented by the numbers outside the parentheses are called only once at the beginning of the simulation to initialize process streams. Those subroutines represented by the numbers inside the parentheses are part of an iterational loop. For example, after XEQ008 and XEQ001 (equipment numbers 15 and 7) are called, XEQ009 (equipment number 8) is


XEQ010
(Eq.#05)
5*
Evaporation
6
XEQ002
(Eq.#01)
1
XEQ008
(Eq.#13)
16
XEQ006
(Eq.#14)
19*
XEQ005
(Eq.#06)
7
Sludge
20*
XEQ008
(Eq.#15)
3*
XEQ003
(Eq.#03)
11
XEQ004
(Eq.#02)
2
XEQ008
(Eq.#12)
16*
XEQ008
(Eq.#11)
14*
XEQ009
(Eq.#09)
12
XEQ009
(Eq.#08)
8
Blowdown
13*
1
2
3*
4*
5*
XEQ001
(Eq.#07)
6
7
8
9*
15*
XEQ007
(Eq.#10)
4*
XEQ003
(Eq.#04)
9*
Sludge

Order of Calculations:
1,2,3,4,5,7 (8,9,10,11,
12,13,14,6,15,7)

Figure 3-1. Ash Sluice Model System Configurations and Order of Calculations.

called again, followed by XEQ009 (equipment number 9) and XEQ007 (equipment number 10). This continues until the convergence criteria are met. Of course, if the user does not specify a treatment option (such as reaction tank or softening), the corresponding subroutine will not be called.

3.3 MODEL USE

The purpose of this subsection is to describe the use of the ash sluice system model by discussing the various input data requirements and the associated output provided by the model.

3.3.1 Input Data

The input data requirements for the ash sluice system model are supplied through five types of data cards submitted by the user in the following order:

1. Title Card
2. Executive Series Card
3. Equipment Subroutine Data Cards
4. End of Equipment Data Card
5. Stream Identification Card (optional)

The deck structure is illustrated in Figure 3-2.

3.3.1.1 Title Card—

The title card is always the first card of the input data set. Any string of up to 78 alphanumeric characters may be used to identify the simulation. Every simulation must have a Title Card.

3.3.1.2 Executive Series Card--

The second card in the input data set is the Executive Series Card. This card contains seven option values placed in the first seven columns of the card. The options specified by the user determine the process configuration, the treatment alternatives that are used, and the level of printout that is desired.

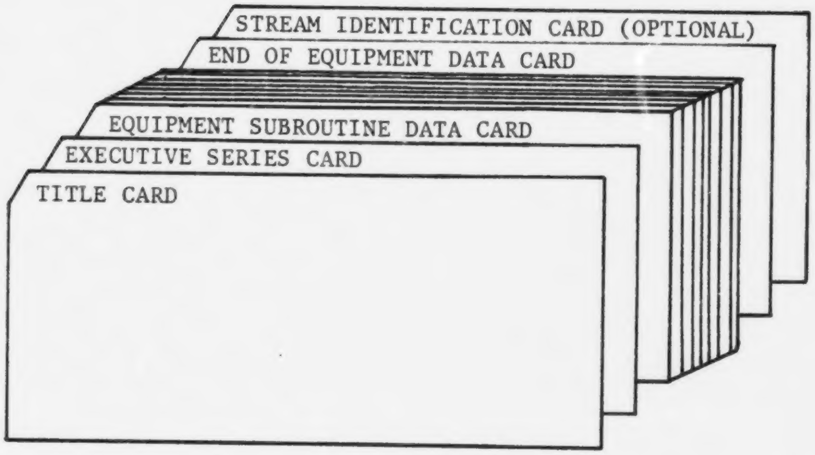

STREAM IDENTIFICATION CARD (OPTIONAL)
END OF EQUIPMENT DATA CARD
EQUIPMENT SUBROUTINE DATA CARD
EXECUTIVE SERIES CARD
TITLE CARD

Figure 3-2. Ash Sluice System Computer Model Deck Structure.

The options are listed below in the order of input:

1. KTRT = treatment alternative
2. KWW = addition of wastewater
3. KAC = convergence parameter for chemical addition
4. KFIX = fixed sidestream treatment rate
5. IOUT = level of printout detail
6. IUNITS = output units
7. ISV = detailed printout of internal streams

The integer values for these variables and option descriptions are presented in Table 3-3. For example, if the user wanted to simulate an existing system with the following characteristics:

- acid/caustic addition,
- wastewater added to pond,
- chemical addition based on user specified pH of recirculating water,

and desired stream output data to be printed for all streams in metric units and a detailed printout of one or more streams, the first seven columns of the Executive Series Card would be 2231122. The specific streams for which the user desires a detailed printout are specified with the Stream Identification Card (see Section 3.3.1.5).

3.3.1.3 Equipment Subroutine Data Cards--

After the Executive Series Card, the data required for the equipment subroutines are input on Equipment Subroutine Data Cards. The equipment subroutines which require data are:

- XEQ002
- XEQ004
- XEQ003
- XEQ010
- XEQ005
- XEQ001
- XEQ007
- XEQ006

TABLE 3-3. EXECUTIVE SERIES INPUT VARIABLES

Variable	Decision	Value	Result
KTRT	Treatment Alternative	1	No treatment
		2	Acid/caustic addition only
		3	Sidestream softening only
		4	Reactor/hold tank only
		5	Acid/caustic with sidestream softening
		6	Acid/caustic with reactor/hold tank
		7	Sidestream softening with reactor/ hold tank
		8	Acid/caustic addition with both sidestream softening and reactor/hold tank
KWW	Use of Wastewater	1	No wastewater added to pond
		2	Wastewater added to pond
KAC	Acid/Caustic Convergence Parameter	1	Acid/caustic addition adjusted to achieve $CaCO_3$ relative saturation specified by user
		2	Acid/caustic addition adjusted to achieve alkalinity specified by user
		3	Acid/caustic addition adjusted to achieve pH specified by user
KFIX	Sidestream Treatment Rate	1	Treatment rate not fixed
		2	Treatment rate fixed
IOUT	Type of Output	1	Stream information printed for all streams in the system at the end of the simulation
		2	Stream information is printed for input and output streams only at the end of the simulation
IUNITS	Output Units	1	English units (Engineering)
		2	Metric units*
ISV	Detailed Printout of Streams	1	No streams specified
		2	Streams specified

*This Option is no longer available.

One or more data cards may be required for each subroutine on the above list. Depending on the type of water treatment selected by the user, certain subroutine data cards may not be required. For instance, unless the user has specified acid/caustic addition or softening treatment, input data for XEQ003 and XEQ007 are unnecessary.

Each subroutine is assigned an equipment number by the ash sluice model, and data are input to the appropriate subroutines by referencing the assigned equipment number. The equipment numbers for each subroutine are presented in Table 3-4.

The input formats for the equipment subroutine data cards are summarized in Figure 3-3. All data, except the equipment number, should be entered as a real number. The required inputs for each equipment subroutine are discussed below.

XEQ002 is called only once at the beginning of the simulation to initialize the ash input stream. The weight fraction input for each species is assumed by the model to completely dissolve. Any portion of the ash not expected to dissolve should be input as inert. XEQ002 requires two data cards. The first card contains the following information:

1. Columns 1-2: Equipment Number
2. Columns 3-10: Ash Temperature, °F
3. Columns 11-20: Calcium, weight fraction dissolving
4. Columns 21-30: Magnesium, weight fraction dissolving
5. Columns 31-40: Sodium, weight fraction dissolving
6. Columns 41-50: Potassium, weight fraction dissolving
7. Columns 51-60: Chloride, weight fraction dissolving
8. Columns 61-70: Sulfate, weight fraction dissolving
9. Columns 71-80: Inerts, weight fraction ash not dissolving

TABLE 3-4. EQUIPMENT SUBROUTINE NUMBERS

Equipment Subroutine	Number
XEQ002	01
XEQ004	02
XEQ003 (when acid/ caustic treatment is specified)	03
XEQ003 (when side-stream softening is specified)	04
XEQ010	05
XEQ005	06
XEQ001	07
XEQ007	10
XEQ006	14

1	3	11	21	31	41	51	61	71
XEQ002 (2 cards)								
01	Temp (°F)	Ca (wt frac)	Mg (wt frac)	Na (wt frac)	K (wt frac)	Cl (wt frac)	SO_4 (wt frac)	Inerts (wt frac)
	Ash flow (lb/min)							
XEQ004 (2 cards)								
02	Temp (°F)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	NH_3 (mg/l)	K (mg/l)	Cl (mg/l)	Alkalinity (mg/l as $CaCO_3$)
	NO_3 (mg/l)	SO_4 (mg/l)	H_4SiO_4 (mg/l)	PO_4 (mg/l)	Suspended Solids (mg/l)	pH	Ion to adjust	
XEQ003 - for acid/caustic treatment (3 cards)								
03	Lime (lb/min)	$Ca(OH)_2$ (wt frac in lime)	$Mg(OH)_2$ (wt frac in lime)	Inerts (wt frac in lime)	Soda Ash (lb/min)	Na_2CO_3 (wt frac in soda ash)	Inerts (wt frac in soda ash)	Magnesium hydroxide (lb/min)
	$Mg(OH)_2$ (wt frac in mag.)	$Ca(OH)_2$ (wt frac in mag.)	Inerts (wt frac in mag.)	Caustic (gal/hr)	NaOH (wt frac in caustic-dry)	Na_2O (wt frac in caustic-dry)	NaCl (wt frac in caustic-dry)	Inerts (wt frac in caustic-dry)
	Caustic Conc. (wt%)	SiO_2 (gal/hr)	Acid (wt%)	Acid type (0.0 H_2SO_4, 1.0 H_2CO_3, 2.0 HCl)				
XEQ003 - for sidestream softening (3 cards)								
04		←SAME AS XEQ003 03→						
		←SAME AS XEQ003 03→						
		←SAME AS XEQ003 03→						
XEQ010 (2 cards)								
05		←SAME AS XEQ004→						
		←SAME AS XEQ004→						Flow rate (gpm)
XEQ005 (1 card)								
06	Evaporation (in/yr)	Solids in pond sludge (wt%)	Pond surface area (acres)	Pond depth (ft)	Pond water temperature (°F)	CO_2 partial pressure of pond water (atm)	Precip. option (0.0 eq, 1.0 no solids, 2.0 rates)	Approach to equilibrium (frac)
XEQ001 (1 card)								
07	System blowdown (gpm)	Solids in ash slurry (wt%)	Desired recirc. pH, alk, RsCaCO$_3$ value	Sidestream flowrate (gpm)				
XEQ007 (2 cards)								
10	Solids in softener sludge (wt%)	Softener residence time (min)	Sludge recycle rate (gpm)	Acid adjust (0.0 pH, 1.0 alk)	Desired pH or alk in return water	$CaCO_3$ carryover (mg/l)	$Mg(OH)_2$ carryover (mg/l)	Lime stoich. factor
	Na_2CO_3 stoich. factor	$Mg(OH)_2$ stoich. factor	Effluent calcium concentration (mg/l)	Approach to equilibrium (frac)	Precipitation (0.0 no rates, 1.0 rate)			
XEQ006 (1 card)								
14	Precip. option (1.0 rate, 2.0 eq, 3.0 no solids)	Tank volume (gal)						

Figure 3-3. Ash Sluice System Computer Model Input Format for Equipment Subroutine Data Cards.

The _second_ _card_ contains the following information:

1. Columns 1-2: Blank
2. Columns 3-10: Ash Flow Rate, lb/min

XEQ004 is also called only once during the simulation. This subroutine is called at the beginning of the simulation to initialize the makeup water stream. Based on the user input composition, pH and temperature values, XEQ004 adjusts an ion to obtain an electrically neutral solution. If no ion is specified by the user, XEQ004 will automatically adjust sodium. XEQ004 requires _two_ _data_ _cards_. The _first_ _card_ contains the following information:

1. Columns 1-2: Equipment Number
2. Columns 3-10: Water Temperature, °F
3. Columns 11-20: Calcium Concentration, mg/l as Ca
4. Columns 21-30: Magnesium Concentration, mg/l as Mg
5. Columns 31-40: Sodium Concentration, mg/l as Na
6. Columns 41-50: Ammonia Concentration, mg/l as NH_3
7. Columns 51-60: Potassium Concentration, mg/l as K
8. Columns 61-70: Chloride Concentration, mg/l as Cl
9. Columns 71-80: Total Alkalinity Concentrations, mg/l as $CaCO_3$

The _second_ _card_ contains the following information:

1. Columns 1-2: Blank
2. Columns 3-10: Nitrate Concentration, mg/l as NO_3
3. Columns 11-20: Sulfate Concentration, mg/l as SO_4
4. Columns 21-30: Silica Concentration, mg/l as SiO_2
5. Columns 31-40: Phosphate Concentration, mg/l as PO_4

6. Columns 41-50: Suspended Solids Concentration, mg/l
7. Columns 51-60: pH
8. Columns 61-70: Ion to adjust to obtain an electrically neutral solution (optional, defaults to sodium)

To specify the ion to be adjusted, the appropriate value is placed in Columns 61-70:

o Calcium	1.0	o Chloride	6.0
o Magnesium	2.0	o Nitrate	7.0
o Sodium	3.0	o Sulfate	9.0
o Ammonia	4.0	o Silica	10.0
o Potassium	5.0	o Phosphate	11.0

The ion specified must have an initial concentration greater than zero.

XEQ003 is required only if the user has specified either acid/caustic addition or sidestream softening as a water treatment. If acid/caustic addition has been specified, XEQ003 initializes the composition and feed rate (if input) for the acid or caustic stream. If sidestream softening has been specified, XEQ003 initializes chemical compositions and feed rates (if input) for lime, soda ash, and magnesium hydroxide. In addition, the composition and flow rate (if input) of sulfuric acid, used to adjust returning softened water, is initialized. This subroutine is not subsequently used in the iterative calculational sequence. XEQ003 requires three data cards. The first card contains the following information:

1. Columns 1-2: Equipment Number
2. Columns 3-10: Lime Flow Rate, lb/min (optional)
3. Columns 11-20: $Ca(OH)_2$ in Lime, weight fraction
4. Columns 21-30: $Mg(OH)_2$ in Lime, weight fraction
5. Columns 31-40: Inert in Lime, weight fraction

6. Columns 41-50: Soda Ash Flow Rate, lb/min (optional)

7. Columns 51-60: Na_2CO_3 in Soda Ash, weight fraction

8. Columns 61-70: Inert in Soda Ash, weight fraction

9. Columns 71-80: Magnesium Additive Flow Rate, lb/min (optional)

The second card contains:

1. Columns 1-2: Blank

2. Columns 3-10: $Mg(OH)_2$ in Magnesium Additive, weight fraction

3. Columns 11-20: $Ca(OH)_2$ in Magnesium Additive, weight fraction

4. Columns 21-30: Inert in Magnesium Additive, weight fraction

5. Columns 31-40: Caustic Flow Rate, gal/hr (optional)

6. Columns 41-50: NaOH in Caustic, weight fraction-dry

7. Columns 51-60: Na_2O in Caustic, weight fraction-dry

8. Columns 61-70: NaCl in Caustic, weight fraction-dry

9. Columns 71-80: Inert in Caustic, weight fraction-dry

The third card contains:

1. Columns 1-2: Blank

2. Columns 3-10: Concentration of Caustic, weight percent

3. Columns 11-20: Sulfuric Acid, gal/hr

4. Columns 21-30: Concentration of Sulfuric Acid, weight percent

5. Columns 31-40: Type of Acid used; 0.0 - sulfuric;
   1.0 = carbonic; 2.0 = hydrochloric

If a specific chemical will not be used for the simulation, it is unnecessary to input a composition for that chemical. However, even if a card contains no data it must be included in the data set.

XEQ010 is required if a wastewater stream is added to the pond. It is used at the beginning of the simulation to initialize the temperature, composition, and flow rate of the wastewater stream. The input format for XEQ010 is identical to that used for XEQ004 except that the flow rate of the stream must be provided. The flow rate is input as gpm on the second XEQ010 data card, Columns 71-80.

XEQ005 is used at the beginning of each simulation to calculate the quantity of water lost through pond evaporation. XEQ005 is also used during the iterative calculational sequence to determine the CO_2 transfer and solid precipitation occurring in the pond and to calculate water occluded with the solids settling in the pond. XEQ005 requires one data card with the following information:

1. Columns 1-2: Equipment Number
2. Columns 3-10: Net Evaporation, inches/year
3. Columns 11-20: Solids in Pond Bottom Sludge, weight percent
4. Columns 21-30: Pond Surface Area, acres
5. Columns 31-40: Pond Depth, ft.
6. Columns 41-50: Pond Water Temperature, °F
7. Columns 51-60: CO_2 Partial Pressure in Pond Water, atm
8. Columns 61-70: Solids Precipitation Option,
   0.0 pond at solid/liquid equilibrium
   1.0 no solids formation allowed
   2.0 rate determined
9. Columns 71-80: Approach to $CaCO_3$ Solid/Liquid Equilibrium, fraction

If no CO_2 transfer is anticipated between the pond and the atmosphere, the partial pressure of CO_2 (Columns 51-60) should be input as 0.0. If a fractional approach to solid/liquid equilibrium is specified in Columns 71-80, information in Columns 61-70 will be ignored.

XEQ001 is used at the beginning of each simulation to initiate flow rate estimates for required makeup water, recirculating water, and acid/caustic addition, if specified. XEQ001 also estimates an initial composition for the system blowdown. During subsequent calls, XEQ001 updates the makeup water and acid/caustic flow rates and the blowdown composition. These updated values are based on an overall mass balance of key species for the ash sluice system. XEQ001 requires one card containing the following information:

1. Columns 1-2: Equipment Number
2. Columns 3-10: Blowdown Flow Rate, gpm
3. Columns 11-20: Solids in Ash Slurry, weight percent
4. Columns 21-30: Desired Recirculating Water $CaCO_3$ Relative Saturation, Alkalinity, or pH Value
5. Columns 31-40: Sidestream Flow Rate, gpm (optional)

XEQ007 is used only if the user has specified sidestream softening as a water treatment option. XEQ007 simulates a single-stage lime or lime/soda ash softener. This subroutine is used during the iterative calculational sequence to determine the sidestream treatment rate (if not specified), the chemical addition rates (if not specified), and the flow rates and compositions of the softener product and sludge blowdown. XEQ007 requires two data cards. The first card contains the following information:

1. Columns 1-2: Equipment Number
2. Columns 3-10: Solids in Softener Sludge, weight percent
3. Columns 11-20: Residence Time, min.
4. Columns 21-30: Sludge Recycle Rate, gpm
5. Columns 31-40: Acid Adjust for Softener Product;
   0.0 adjust to achieve pH
   1.0 adjust to achieve alkalinity
6. Columns 41-50: Desired pH or Alkalinity Value
   (alkalinity in mg/l as $CaCO_3$)

7. Columns 51-60: $CaCO_3$ Carryover, mg/l

8. Columns 61-70: $Mg(OH)_2$ Carryover, mg/l

9. Columns 71-80: Lime Stoichiometric Factor

The second card contains:

1. Columns 1-2: Blank

2. Columns 3-10: Soda Ash Stoichiometric Factor

3. Columns 11-20: Magnesium Hydroxide Stoichiometric Factor

4. Columns 21-30: Desired Effluent Calcium Concentration (optional)

5. Columns 31-40: Approach to Solid-Liquid Equilibrium, fraction (optional)

6. Columns 41-50: Solids Precipitation;
   0.0 = solid-liquid equilibrium assumed,
   1.0 = precipitation rates used (optional)

Only one of items 4 through 6 listed on the second card must be specified. Stoichiometric factors are required only if chemical addition rates are not specified in XEQ003.

The method used to calculate the required chemicals in XEQ007 is based on recommended dosages outlined in the Permutit Data Book (4). For a stoichiometric factor of 1.0, the recommended dosage is added by the model. For a factor of 2.0, twice the recommended dosage is added.

XEQ006 is used if reaction/hold tank is specified. XEQ006 calculates the quantity of solids precipitating in a reaction/hold tank. One card is required by XEQ006 containing the following information:

1. Columns 1-3: Equipment Number

2. Columns 4-10: Solid Precipitation Option;
   1.0 precipitation rates used,
   2.0 solid-liquid equilibrium assumed

3. Columns 11-20: Tank Volume, gal.

The data card(s) for each equipment subroutine used during the simulation should be included as a set following the Executive Series card. The overall order of the equipment data card sets does not matter, since each set of data is identified with an equipment number. However, if an equipment subroutine requires more than one data card, these cards must be placed in the proper order if the process model is to correctly interpret the input information.

3.3.1.4 End of Equipment Data Card—

The End of Equipment Data Card contains 99 in the first two columns of the card. Any cards following the End of Equipment Data Card will be ignored unless ISV (on the Executive Series Card) has been set equal to 2. In that case, the Stream Identification Card will be read.

3.3.1.5 Stream Identification Card—

If the user has specified a detailed printout of a stream, the card following the End of Equipment Data Card is used to request a complete stream vector listing for any number of streams from 1 to 25. The stream numbers for which the detailed listing is desired are listed as 3-digit integers on the card, with no punctuation separating them. For instance, if the user desired a complete stream vector listing for streams 1, 8, 15, and 22, the Stream Identification Card would be as follows, beginning in Column 1: 001008015022. (Refer to Figure 3-1 for stream numbers.)

3.4 INTERPRETATION OF RESULTS

This discussion focuses on the results of a series of simulation cases. These cases are intended to demonstrate the use of the ash sluice model as a tool to aid in the design or operation of an ash sluice system. The first case (base case) represents a system in which water treatment is not used. This is followed by three simulations of the same system using some type of water treatment (acid addition, the incorporation of a reaction/hold tank, and sidestream softening). These cases represent possible options to reduce the potential for scale formation in the recirculating stream.

The computer model provides the user with several types of output, including:

- a process description,
- an echo print of the input data,
- summary information tables,
- detailed stream information tables,
- stream vector listing (optional), and
- warning and error messages.

The files used as input for the four example cases are included in Appendix B.

3.4.1 Base Case

The base case conditions are outlined in Table 3-5. Ash is sluiced at a rate of 25,000 lb/hr (3.15 kg/s) in a 9.0 weight percent slurry. The blowdown flow rate is 40.0 gpm (152 lpm). No recirculating water treatment is specified.

The first item printed is the process description. As shown in Table 3-6, each equipment subroutine and its appropriate number are listed, along with the stream numbers for all inlet and outlet streams. As part of the process description, the order of calculations and a word description of the system being simulated are also printed.

After the process description, the process model provides an echo print of the input data. This allows the user to verify that the information was input correctly. In Table 3-7, the input data associated with the equipment subroutines for the base case are presented.

As the process model performs iterative calculations around the ash sluice loop, a summary information table is printed after each call to XEQ001. The final summary table represents the converged system values. An example of

TABLE 3-5. BASE CASE CONDITIONS

Parameter	Value
Ash Rate (lb/hr)	25,000 (3.15 kg/s)
Slurry Solids (wt%)	9.0
Quantity Species Leaching from Ash (wt%)	
Calcium	0.481
Magnesium	0.001
Sodium	0.003
Potassium	0.002
Chloride	0.000
Sulfate	0.302
Blowdown Flow Rate (gpm)	40.0 (152 lpm)
Makeup Water Composition (mg/l)	
Calcium	44.1
Magnesium	13.0
Sodium	10.0
Potassium	0.8
Chloride	1.0
Alkalinity (as $CaCO_3$)	145.0
Sulfate	38.1
pH	9.8
Temperature (°F)	62.0
Net Annual Evaporation (in in.)	3.0

TABLE 3-6. SAMPLE PROCESS DESCRIPTION PRINTOUT

```
        EXAMPLE CASE 1: NO TREATMENT, NO CO2 TRANSFER, NO SOLIDS IN POND

                      PROCESS DESCRIPTION

EQUIP.NO.        EQUIP.NAME       INPUT STREAMS            OUTPUT STREAMS

    1              XEQ002       0   0   0   0   0      1   0   0   0   0
    2              XEQ004       0   0   0   0   0      2   0   0   0   0
    3                           0   0   0   0   0      0   0   0   0   0
    4                           0   0   0   0   0      0   0   0   0   0
    5                           0   0   0   0   0      0   0   0   0   0
    6              XEQ005      18   0   0   0   0      6   7  11   0   0
    7              XEQ001       1   2   0   0   0      6   7   8   0   0
    8              XEQ009      11   0   0   0   0      8  12   0   0   0
    9                           0   0   0   0   0      0   0   0   0   0
   10                           0   0   0   0   0      0   0   0   0   0
   11                           0   0   0   0   0      0   0   0   0   0
   12              XEQ008       2  12   0   0   0     17   0   0   0   0
   13              XEQ008       1  17   0   0   0     18   0   0   0   0
   14                           0   0   0   0   0      0   0   0   0   0
   15                           0   0   0   0   0      0   0   0   0   0

                  ORDER OF PROCESS CALCULATIONS

         1, 2, 7( 8,12,13, 6, 7)

         RECYCLE LOOP FROM  8 TO  7

         NO TREATMENT SPECIFIED

         NO WASTEWATER ADDED TO POND FROM OUTSIDE SOURCE
```

TABLE 3-7. SAMPLE ECHO PRINT OF INPUT DATA

```
                               EXAMPLE CASE 1: NO TREATMENT, NO CO2 TRANSFER, NO SOLIDS IN POND
SYSTEM AND EQUIPMENT PARAMETERS


   XEQ002, EQUIPMENT NUMBER  1
     ASH FLOW RATE =   .4167+003 LB/MIN
     TEMPERATURE = 120.0 DEG F

       SPECIES          WT. %        SPECIES          WT. %
       CA++              .487        K+                .002
       MG++              .001        CL-               .000
       NA+               .003        SO4--             .302
       INERT           99.103        SIO2              .000



    XEQ004, EQPT. NO.  2
     MAKEUP WATER INPUT DATA
       ION        SPECIES          CONCENTRATION, PPM     ION          SPECIES            CONCENTRATION, PPM
        1    CALCIUM (AS CA)                 44.1          7    ALKALINITY (AS CACO3)          145.0
        2    MAGNESIUM (AS MG)               13.0          8    NITRATE (AS NO3)                  .0
        3    SODIUM (AS NA)                  10.0          9    SULFATE (AS SO4)                38.1
        4    AMMONIA (AS NH4)                  .0          10   SILICA (AS SIO2)                  .0
        5    POTASSIUM (AS K)                  .8          11   PHOSPHATE (AS PO4)                .0
        6    CHLORIDE (AS CL)                 1.0          12   SUS. SOLIDS                       .0
        ION NO.  3 ADJUSTED TO       9.8 PPM TO MINIMIZE ION IMBALANCE
        TEMPERATURE =  62.0 DEG. F
        PH =  8.00
```

(Continued)

TABLE 3-7. (Continued)

```
                                       EXAMPLE CASE 1: NO TREATMENT, NO CO2 TRANSFER, NO SOLIDS IN POND
SYSTEM AND EQUIPMENT PARAMETERS

   XEQ001, EQUIPMENT NUMBER 7

    SPECIFIED BLOWDOWN RATE =     40.000 GPM
    SOLIDS IN ASH SLURRY =  9.00 WT. PERCENT


   XEQ005, EQUIPMENT NUMBER 6

    NET ANNUAL EVAPORATION =   3.0 INCHES
    WT. PERCENT SOLIDS IN POND BOTTOM SLUDGE =  50.0
    POND SURFACE AREA =   5.00 ACRES
    APPROXIMATE POND DEPTH =  10.0 FT
    POND WATER TEMPERATURE =  75.0 DEG F
    NO SOLIDS FORMATION ALLOWED IN POND
```

the summary information table is shown in Table 3-8. The summary print includes flow and composition information for the major process streams. In addition, the relative saturation values for gypsum and calcium carbonate are presented for both the blowdown stream and the ash slurry stream.

The relative saturation values calculated for the blowdown stream are of primary importance, since this composition is the same as the recirculating stream composition. Relative saturation values greater than 1.0 indicate that a stream is supersaturated for a particular species, and the potential for solids formation exists. To insure scale-free operation of an ash sluice system, the relative saturation values of all potential scale-forming species should be less than 1.0 in the recirculating water stream.

The calculated calcium carbonate relative saturation value is extremely high (>300) in the blowdown stream, indicating a high potential for calcium carbonate scale formation. The calculated gypsum relative saturation value is also greater than 1.0, indicating that gypsum may also precipitate in the recirculating line.

At the bottom of the summary table, the convergence parameter is printed. This value is the sum of the change in the blowdown concentration of each species from one iteration to the next and must be less than 0.015 for convergence to be achieved. A minimum of four iterations is completed during a simulation, regardless of the convergence parameter value.

After the case has converged or 16 iterations have been completed without convergence, a detailed stream information table is printed. This is shown in Table 3-9. This table presents more detailed information including the compositions and flow rates of the internal streams.

In cases where the user is having difficulty getting a case to converge or would like to know the specific chemical distribution for a particular stream, a stream vector listing may be desired. To obtain a stream vector

TABLE 3-8. SUMMARY INFORMATION TABLE--BASE CASE, NO TREATMENT

```
                             SUMMARY OF RECIRCULATING ASH SLUICE WATER OPERATION

                   LIQUID INPUTS                                                  LIQUID OUTPUTS
**************************************************    *************************************
COMPONENT     MAKEUP       ADDITIONAL    ACID/CAUSTIC        POND        SYSTEM       SOFTENER
  (PPM)        WATER       WASTEWATER      ADDITION          SLUDGE      BLOWDOWN      SLUDGE

 CA             44.1           .0              .0           2714.8      2714.8           .0
 MG             13.0           .0              .0             18.7        18.7           .0
 NA              9.8           .0              .0             26.6        26.6           .0
 NH4              .0           .0              .0               .0          .0           .0
 K                .8           .0              .0             11.9        11.9           .0
 CL              1.0           .0              .0              1.0         1.0           .0
 ALK           145.0           .0              .0           5141.2      5141.2           .0
 NO3              .0           .0              .0               .0          .0           .0
 SO4            38.1           .0              .0           1715.1      1715.1           .0
 SIO2             .0           .0              .0               .0          .0           .0
 PO4              .0           .0              .0               .0          .0           .0
 INERTS           .0           .0              .0               .0          .0           .0
 FLOW (GPM)     90.7           .0            .000             50.1        40.0           .0
 PH              8.0           .0              .0             12.8        12.8           .0
 RS CACO3       1.05          .00                           305.24      305.24
 RS GYPSUM       .01          .00                             1.46        1.46
 RS GYPSUM IN ASH SLURRY STREAM =    1.46
 RS CACO3 IN ASH SLURRY STREAM =  304.55

                          SOLID INPUTS                                SOLID OUTPUTS
         ***********************************************      *********************
         COMPONENT      ASH      COMPONENT     SOFTENER          POND       SOFTENER
           (WT%)       INPUT       (WT%)       CHEMICALS         SLUDGE      SLUDGE

         CA             .48      CA(OH)2           .00             .00         .00
         MG             .00      CACO3             .00             .00         .00
         NA             .00      CA3(PO4)2         .00             .00         .00
         NH4            .00      CASO4(ANH)        .00             .00         .00
         K              .00      CASO4.2H2O        .00             .00         .00
         CL             .00      MG(OH)2           .00             .00         .00
         NO3            .00      MGCO3.2H2O        .00             .00         .00
         SO4            .30      SEPIOLITE         .00             .00         .00
         SIO2           .00      CAH2SIO4          .00             .00         .00
         PO4            .00      SIO2              .00             .00         .00
         INERTS       99.10      CAHPO4            .00             .00         .00
         FLOW (LB/HR) 25004.     NA2CO3            .00             .00         .00
                                 INERTS            .00          100.00         .00
                                 FLOW (LB/HR)      .00          25000.          .0

XC0004 LOOP NO.  4       VALUE OF FUNCTION =   .51479-002
```

TABLE 3-9. DETAILED STREAM INFORMATION--BASE CASE, NO TREATMENT

```
                                DETAILED RECIRCULATING ASH SLUICE WATER INPUT    STREAMS

STREAM ID,UNITS                                         STREAM  NUMBER
                                 ------------------------------------------------------------------------
                                    1                2                3                4                5
                                 ------------------------------------------------------------------------
TEMPERATURE,  DEG F       .1200+003        .6200+002
PRESSURE,     PSIA                         .1470+002

TOT GAS FLOW  LB/HR
MOLE %   N2
         O2
         H2O
         CO2
 DUST, DRY    GR/SCF

TOTAL LIQUID   GPM                         .9667+002
               LB/HR                       .4536+005
   CA         PPM                          .4411+002
   MG                                      .1300+002
   NA                                      .9832+001
   NH4
   K                                       .8[illegible]19+000
   CL                                      .9999+000
   CO3                                     .1758+003
   NO3
   SO4                                     .3812+002
   SIO2
   PO4
   TDS                                     .2826+003
SUS SOL WT %
PH                                         .8001+001
R.S. GYPSUM                                .8011-002
      CACO3                                .1050+001
      MG(OH)2
IONIC STR.                                 .5441-002

TOT SOLIDS     LB/HR      .2500+005
  CA(OH)2     WT. %
  CACO3
  CA3(PO4)2
  CASO4,ANH
  CASO4,GYP
  MG(OH)2
  MGCO3.5H2O
  SEPIOLITE
  CAH2SIO4
  SIO2
  CAHPO4
  NA2CO3
  INERT                   .1000+003
```

TABLE 3-9. (Continued)

```
                            DETAILED RECIRCULATING ASH SLUICE WATER OUTPUT   STREAMS

STREAM ID,UNITS                                     STREAM  NUMBER
                         ------------------------------------------------------------------
                              6            7            8            9            10
                         ------------------------------------------------------------------
TEMPERATURE,  DEG F      .7500+002    .7500+002    .7500+002
PRESSURE,     PSIA

TOT GAS FLOW  LB/HR      .3871+003
MOLE %   N2
         O2
         H2O             .1000+003
         CO2
 DUST, DRY    GR/SCF

TOTAL LIQUID   GPM                    .5006+002    .3997+002
               LB/HR                  .2512+005    .2006+005
   CA         PPM                     .2719+004    .2719+004
   MG                                 .1868+002    .1868+002
   NA                                 .2660+002    .2660+002
   NH4
   K                                  .1193+002    .1193+002
   CL                                 .1009+001    .1009+001
   CO3                                .1773+003    .1773+003
   NO3
   SO4                                .1718+004    .1718+004
   SIO2
   PO4
   TDS                                .4672+004    .4672+004
SUS SOL WT %                          .4988+002
PH                                    .1279+002    .1279+002
R.S. GYPSUM                           .1463+001    .1463+001
     CACO3                            .3052+003    .3052+003
     MG(OH)2
IONIC STR.                            .1514+000    .1514+000

TOT SOLIDS     LB/HR                  .2500+005
  CA(OH)2     WT. %
  CACO3
  CA3(PO4)2
  CASO4,ANH
  CASO4,GYP
  MG(OH)2
  MGCO3.5H2O
  SEPIOLITE
  CAH2SIO4
  SIO2
  CAHPO4
  NA2CO3
  INERT                               .1000+003
```

TABLE 3-9. (Continued)

DETAILED RECIRCULATING ASH SLUICE WATER INTERNAL STREAMS

STREAM ID,UNITS		STREAM NUMBER 11	12	13	14	15	16
TEMPERATURE,	DEG F	.7500+002	.7500+002	.7500+002			
PRESSURE,	PSIA						
TOT GAS FLO-	LB/HR						
MOLE % N2							
O2							
H2O							
CO2							
DUST, DRY	GR/SCF						
TOTAL LIQUID	GPM	.4524+003	.4132+003	.9106+002			
	LB/HR	.2270+006	.2073+006	.4547+005			
CA	PPM	.2719+004	.2717+004				
MG		.1868+002	.1867+002				
NA		.2660+002	.2658+002				
NH4							
K		.1193+002	.1192+002				
CL		.1009+001	.1008+001				
CO3		.1773+003	.1772+003				
NO3							
SO4		.1718+004	.1716+004				
SIO2							
PO4							
TDS		.4672+004	.4669+004				
SUS SOL WT %							
PH		.1279+002	.1279+002				
R.S. GYPSUM		.1463+001	.1462+001				
CACO3		.3052+003	.3050+003				
MG(OH)2							
IONIC STR.		.1514+000	.1513+000				
TOT SOLIDS	LB/HR						
CA(OH)2	WT. %						
CACO3							
CA3(PO4)2							
CASO4,ANH							
CASO4,GYP							
MG(OH)2							
MGCO3.5H2O							
SEPIOLITE							
CAH2SIO4							
SIO2							
CAHPO4							
NA2CO3							
INERT							

TABLE 3-9. (Continued)

DETAILED RECIRCULATING ASH SLUICE WATER INTERNAL STREAMS

STREAM ID,UNITS		STREAM NUMBER					
		17	18	19	20	21	22
TEMPERATURE,	DEG F	.7500+002	.7500+002				
PRESSURE,	PSIA						
TOT GAS FLOW	LB/HR						
MOLE % N2							
O2							
H2O							
CO2							
DUST, DRY	GR/SCF						
TOTAL LIQUID	GPM	.5040+003	.5036+003				
	LB/HR	.2527+006	.2527+006				
CA	PPM	.2237+004	.2713+004				
MG		.1765+002	.1864+002				
NA		.2357+002	.2654+002				
NH4							
K		.9925+001	.1190+002				
CL		.1007+001	.1006+001				
CO3		.1769+003	.1769+003				
NO3							
SO4		.1415+004	.1714+004				
SIO2							
PO4							
TDS		.3881+004	.4662+004				
SUS SOL WT %			.9001+001				
PH		.1193+002	.1279+002				
R.S. GYPSUM		.1200+001	.1460+001				
CACO3		.2502+003	.3045+003				
MG(OH)2							
IONIC STR.		.1250+000	.1511+000				
TOT SOLIDS	LB/HR		.2500+005				
CA(OH)2	WT. %						
CACO3							
CA3(PO4)2							
CASO4,ANH							
CASO4,GYP							
MG(OH)2							
MGCO3.5H2O							
SEPIOLITE							
CAH2SIO4							
SIO2							
CAHPO4							
NA2CO3							
INERT			.1000+003				

listing, a Stream Identification Card must be included in the input data set as discussed previously.

3.4.2 Acid Addition

In the second case a 50 weight percent hydrochloric acid solution was added by the model to adjust the recirculating pH to 7.5. The final summary table for this case is presented in Table 3-10. Note that the required acid addition rate is included in the summary table.

Although the relative saturation of calcium carbonate has been reduced significantly, the gypsum relative saturation value is still greater than 1.0 as would be expected. This indicates that additional water treatment would be required to reduce the scaling potential of gypsum in the recirculating water stream.

3.4.3 Reaction/Hold Tank

In the third case, the effect of a hold tank on the recirculating water composition is simulated. The model uses precipitation rate equations based on the driving force for precipitation (relative saturation) and the available crystal surface area to calculate the quantity of material precipitating in the reaction tank. The constants for each precipitating species were developed in the laboratory and have not been verified with actual ash sluice system field data. This should be considered for simulation cases involving a hold tank.

As discussed previously, the hold tank provides additional ash mixing time to encourage supersaturated species to precipitate on the ash, thus reducing the potential for precipitation in the recirculating system.

TABLE 3-10. SUMMARY INFORMATION TABLE--EXAMPLE CASE 2, ACID ADDITION

```
                          SUMMARY OF RECIRCULATING ASH SLUICE WATER OPERATION

                    LIQUID INPUTS                                               LIQUID OUTPUTS
**************************************************************     ****************************************
COMPONENT        MAKEUP       ADDITIONAL       ACID/CAUSTIC         POND          SYSTEM        SOFTENER
  (PPM)           WATER       WASTEWATER         ADDITION          SLUDGE        BLOWDOWN        SLUDGE

 CA               44.1             .0                .0            2711.7         2710.2             .0
 MG               13.0             .0                .0              18.6           18.6             .0
 NA                9.8             .0                .0              26.5           26.5             .0
 NH4                .0             .0                .0                .0             .0             .0
 K                  .8             .0                .0              11.9           11.9             .0
 CL                1.0             .0          500049.4            2907.4         3534.7             .0
 ALK             145.0             .0                .0            1032.7          144.6             .0
 NO3                .0             .0                .0                .0             .0             .0
 SO4              38.1             .0                .0            1713.0         1712.1             .0
 SIO2               .0             .0                .0                .0             .0             .0
 PO4                .0             .0                .0                .0             .0             .0
 INERTS             .0             .0                .0                .0             .0             .0
 FLOW (GPM)       90.4             .0              .583              50.1           40.0             .0
 PH                8.0             .0                .0              11.9            7.5             .0
 RS CACO3         1.05            .00                              312.94           7.64
 RS GYPSUM         .01            .00                                1.70           1.75
 RS GYPSUM IN ASH SLURRY STREAM =    1.69
 RS CACO3 IN ASH SLURRY STREAM =   312.41

                          SOLID INPUTS                                     SOLID OUTPUTS
           ************************************************          ***********************
           COMPONENT      ASH       COMPONENT       SOFTENER            POND       SOFTENER
             (WT%)       INPUT        (WT%)        CHEMICALS           SLUDGE       SLUDGE

           CA              .43      CA(OH)2              .00              .00          .00
           MG              .00      CACO3                .00              .00          .00
           NA              .00      CA3(PO4)2            .00              .00          .00
           NH4             .00      CASO4(ANH)           .00              .00          .00
           K               .00      CASO4.2H2O           .00              .00          .00
           CL              .00      MG(OH)2              .00              .00          .00
           NO3             .00      MGCO3.2H2O           .00              .00          .00
           SO4             .30      SEPIOLITE            .00              .00          .00
           SIO2            .00      CAH2SIO4             .00              .00          .00
           PO4             .00      SIO2                 .00              .00          .00
           INERTS        99.10      CAHPO4               .00              .00          .00
           FLOW (LB/HR) 25004.      NA2CO3               .00              .00          .00
                                    INERTS               .00           100.00          .00
                                    FLOW (LB/HR)         .00           25000.           .0

XC0004 LOOP NO.  4        VALUE OF FUNCTION =    .15268-002
```

For the example case, a 100 gallon reaction/hold tank was used. The final summary table is shown in Table 3-11. Based on the model's rate information, the hold time provided by the tank was sufficient for both calcium carbonate and gypsum to reach solid/liquid equilibrium (relative saturation near 1.0).

3.4.4 Sidestream Softening

An additional treatment option is to soften a portion or all of the water prior to being recirculated. For the example case, softening chemicals (lime and soda ash) were added at stoichiometric dosages at 1.0 each. Dosages used by the model include: one equivalent of lime for each unit of calcium alkalinity removed, two equivalents of lime for each unit of magnesium alkalinity removed, and one equivalent of soda ash for each unit of calcium noncarbonate hardness removed. These are outlined in the Permutit Data Book (4). A treatment rate of 250 gpm was specified to reduce the recirculating gypsum relative saturation. The summary print table for sidestream softening cases includes the required chemical addition rate and the sludge production rate and composition.

As shown in Table 3-12, a treatment rate of 250 gpm (approximately 64 percent of recirculating flow rate) was required to reduce the gypsum relative saturation to a value near 1.0. In this case, pH adjustment of the recirculating water would also be required to reduce the relative saturation of calcium carbonate.

3.4.5 Warning and Error Messages

Warning and error messages are provided by the model when there is some difficulty with the simulation. Warning messages usually let the user know that a treatment that has been specified is not needed or that a treatment option should be considered. In most cases, the simulation is not terminated because of a warning message. Error messages indicate that the simulation cannot be completed and computation is terminated. These usually result from

TABLE 3-11. SUMMARY INFORMATION TABLE--EXAMPLE CASE 3, REACTION HOLD TANK

```
                        SUMMARY OF RECIRCULATING ASH SLUICE WATER OPERATION

                     LIQUID INPUTS                                    LIQUID OUTPUTS
 ******************************************************    **************************************
  COMPONENT     MAKEUP   ADDITIONAL      ACID/CAUSTIC         POND       SYSTEM     SOFTENER
   (PPM)         WATER   WASTEWATER        ADDITION         SLUDGE     BLOWDOWN      SLUDGE

  CA               44.1            .0             .0          1310.1      1310.1          .0
  MG               13.0            .0             .0              .0          .0          .0
  NA                9.8            .0             .0            26.6        26.6          .0
  NH4               .0            .0             .0              .0          .0          .0
  K                  .8            .0             .0            11.9        11.9          .0
  CL                1.0            .0             .0             1.0         1.0          .0
  ALK             145.0            .0             .0          2035.4      2035.4          .0
  NO3               .0            .0             .0              .0          .0          .0
  SO4              38.1            .0             .0          1255.4      1255.4          .0
  SIO2              .0            .0             .0              .0          .0          .0
  PO4               .0            .0             .0              .0          .0          .0
  INERTS            .0            .0             .0              .0          .0          .0
  FLOW (GPM)       91.0            .0           .000            50.3        40.0          .0
  PH                8.0            .0             .0            12.5        12.5          .0
  RS CACO3         1.05           .00                           1.01         1.01
  RS GYPSUM         .01           .00                           1.00         1.00
  RS GYPSUM IN ASH SLURRY STREAM =    1.09
  RS CACO3 IN ASH SLURRY STREAM =    56.87

                            SOLID INPUTS                             SOLID OUTPUTS
          *************************************************      **********************
           COMPONENT      ASH       COMPONENT   SOFTENER           POND     SOFTENER
            (WT%)        INPUT       (WT%)      CHEMICALS         SLUDGE     SLUDGE

           CA              .48     CA(OH)2             .00             .36         .00
           MG              .00     CACO3               .00             .05         .00
           NA              .00     CA3(PO4)2           .00             .00         .00
           NH4             .00     CASO4(ANH)          .00             .00         .00
           K               .00     CASO4.2H2O          .00             .15         .00
           CL              .00     MG(OH)2             .00             .01         .00
           NO3             .00     MGCO3.2H2O          .00             .00         .00
           SO4             .30     SEPIOLITE           .00             .00         .00
           SIO2            .00     CAH2SIO4            .00             .00         .00
           PO4             .00     SIO2                .00             .00         .00
           INERTS        99.10     CAHPO4              .00             .00         .00
           FLOW (LB/HR) 25004.     NA2CO3              .00             .00         .00
                                   INERTS              .00           99.43         .00
                                   FLOW (LB/HR)        .00          25144.          .0

XC0004 LOOP NO.  4       VALUE OF FUNCTION =   .15086-002
```

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TABLE 3-12. SUMMARY INFORMATION TABLE--EXAMPLE CASE 4, SIDESTREAM SOFTENING

```
                                 SUMMARY OF RECIRCULATING ASH SLUICE WATER OPERATION

                       LIQUID INPUTS                                               LIQUID OUTPUTS
*****************************************************************     ************************************************
 COMPONENT        MAKEUP      ADDITIONAL     ACID/CAUSTIC            POND          SYSTEM         SOFTENER
  (PPM)           WATER       WASTEWATER       ADDITION              SLUDGE        BLOWDOWN        SLUDGE

 CA                44.1             .0               .0               747.6          747.6            39.9
 MG                13.0             .0               .0                 7.5            7.5              .2
 NA                 9.8             .0               .0               978.5          978.5          1758.5
 NH4                 .0             .0               .0                  .0             .0              .0
 K                   .8             .0               .0                 7.4            7.4             7.4
 CL                 1.0             .0               .0                 1.0            1.0             1.0
 ALK              145.0             .0               .0              1413.3         1413.3          1299.9
 NO3                 .0             .0               .0                  .0             .0              .0
 SO4               38.2             .0               .0              2516.7         2516.7          2530.6
 SIO2                .0             .0               .0                  .0             .0              .0
 PO4                 .0             .0               .0                  .0             .0              .0
 INERTS              .0             .0               .0                  .0             .0              .0
 FLOW (GPM)       153.4             .0             .000                50.1           40.0            62.8
 PH                 8.0             .0               .0                12.3           12.3              .0
 RS CACO3          1.05            .00                               114.28         114.28
 RS GYPSUM          .01            .00                                 1.06           1.06
 RS GYPSUM IN ASH SLURRY STREAM =    1.05
 RS CACO3 IN ASH SLURRY STREAM =  114.07

                           SOLID INPUTS                                          SOLID OUTPUTS
        ***************************************************              **********************
         COMPONENT        ASH        COMPONENT      SOFTENER                 POND      SOFTENER
           (WT%)         INPUT         (WT%)        CHEMICALS                SLUDGE     SLUDGE

         CA                .48      CA(OH)2              .13                  .00         .00
         MG                .00      CACO3                .00                  .00       99.03
         NA                .00      CA3(PO4)2            .00                  .00         .00
         NH4               .00      CASO4(ANH)           .00                  .00         .00
         K                 .00      CASO4.2H2O           .00                  .00         .00
         CL                .00      MG(OH)2              .00                  .00         .97
         NO3               .00      MGCO3.2H2O           .00                  .00         .00
         SO4               .30      SEPIOLITE            .00                  .00         .00
         SIO2              .00      CAH2SIO4             .00                  .00         .00
         PO4               .00      SIO2                 .00                  .00         .00
         INERTS          99.10      CAHPO4               .00                  .00         .00
         FLOW (LB/HR) 25004.        NA2CO3             99.87                  .00         .00
                                    INERTS               .00               100.00         .00
                                    FLOW (LB/HR)      223.77               25000.       224.2

         SOFTENER OPERATING DATA

            TREATMENT RATE =    249.8 GPM
            INLET CA CONCENTRATION  =   747.56 PPM
            OUTLET CA CONCENTRATION =    39.87 PPM
XC0004 LOOP NO. 12      VALUE OF FUNCTION =   .14401-001
```

the user specifying a condition that cannot be met. Examples of this are the specified blowdown flow rate being greater than the recirculating flow rate or the specified pond sludge weight percent solids being less than the weight percent solids in the ash sluice line. In each case, the user must modify the input data.

SECTION 4

PILOT SYSTEM DESIGN AND TESTING

During this program an ash sluice pilot system was developed to simulate operating and chemistry conditions found in ash sluice systems at coal-fired power plants. This system was used for field testing at two power plants to determine limitations that would be encountered during closed-loop operation. Since the formation of inorganic scale was predicted and verified in the field as the most significant limitation, three treatment approaches to control scale formation were also evaluated. A review of the pilot unit design and the field test approach used at each power plant is necessary before field test and computer simulation results can be effectively presented. This section describes the design basis, flexibility, and limitations of the pilot unit, the field testing approach, as well as the results of the tests at each plant. The field test results and computer process model predictions are also compared to demonstrate the capability of the model as a design and problem-solving tool.

4.1 PILOT SYSTEM DESIGN

The design of the ash sluice pilot system was based upon actual power plant operating conditions, bench-scale simulations, and laboratory ash leaching studies. Four potential host plants were visited to collect samples for characterization and to determine ash sluice system design flow rates and retention times. The system was thus designed to duplicate the average flow and mixing conditions found at these plants. A summary of these design conditions is presented in Table 4-1. Three treatment options were incorporated in the pilot unit design. These options included:

TABLE 4-1. ASH SLUICE PILOT SYSTEM DESIGN BASIS

Design Criteria	Design Value	Source of Design Value
Ash slurry transport time (Hydrovactor to the pond)	2 minutes (maximum)	Power plant data
Slurry concentration range	1 - 12 weight percent	Power plant data
Time required for the maximum amount of leaching to occur	10 minutes (maximum)	Bench-scale test data
pH range of ash pond wastes	4 - 11	Power plant data

- providing increased ash/water contact time in a reaction/hold tank prior to sluicing ash,

- pH adjustment of the recirculating water, and

- softening of a sidestream of the recirculating water.

These treatment options were demonstrated to be effective in preventing solids precipitation during the bench-scale ash sluicing system closed-loop simulations.

The only aspect of power plant ash sluicing systems that could not be duplicated by the pilot unit was the long retention time in the ash settling ponds. In a power plant the ash sluice water may be retained in an ash pond for several days or even weeks. During this time the water is exposed to the atmosphere, and transfer of carbon dioxide between the pond water and the atmosphere may occur. CO_2 transfer can affect the water chemistry by increasing the alkalinity concentration, thus encouraging the precipitation of calcium carbonate. Ultimately, CO_2 transfer can lower the pH of the water in alkaline ash ponds. Characterization of influents and effluents from these large volume ash ponds indicated that CO_2 transfer was very low for the plants under consideration. The CO_2 transfer is also very low in the pilot unit because of the limited exposure of the sluice water to the atmosphere. Therefore, the pilot system should provide a simulation of a low CO_2 transfer condition. It should be noted that an evaluation of CO_2 transfer was not within the scope of this study, but is mentioned here to define a limitation in the pilot unit design.

Another major consideration in the design of the system was the approach to steady state chemistry conditions. A system is considered to be at steady-state conditions when the flow rate, temperature, pressure, and chemical composition of individual streams are not changing during continuous operation. The amount of time required to achieve steady state operation (approach to steady state) is a function of many variables, including the leaching rate of soluble components in the fly ash, and retention time of both water and ash in the system. The faster the approach to steady state, the faster a specific set of operating conditions or a particular water treatment alternative can be evaluated. Since the amount of time for field testing at any given site is limited, a system which rapidly approaches steady state was essential in order to evaluate several different continuous operating conditions.

In order for the field test system to rapidly approach steady-state conditions, three criteria were used in the design of the system:

- maximize ash-water reaction time,
- minimize water loss from the system, and
- minimize overall system volume.

The pilot system as originally conceived met all these criteria. The original pilot system conceptual design used a clarifier to separate the ash from the slurry as a simulation of pond settling conditions. The clarifier underflow was dewatered in a filter with the filtrate returned to the system. However, during the detailed design of the field test unit, it became apparent that continuous operation of the clarifier and underflow filter at high slurry concentrations (approaching 10 weight percent ash) would not be possible. At these slurry concentrations, the frequent backwash cycle of the underflow filter required more time than the clarifier sludge blowoff cycle. The inability to properly blowoff the clarifier sludge would limit its performance. The ultimate result would be either operation at reduced flow rates or intermittent operation at design flow rates. Neither of these alternatives was considered satisfactory.

In order to achieve continuous steady-state operation at design capacity, two full flow filter presses were substituted for the clarifier/underflow filter arrangement. The filter presses are operated with one in service while the other is cleaned, thus ensuring continuous operation of the system. In the filter press, the ash is removed from the slurry by impaction on a fine polypropylene membrane. The ash forms a layer on the membrane which increases the contact time with the water as it filters through. This ash layer also acts as a precoat filter media which reduces the potential for scaling of the membrane surface. Although the filter press operation does not physically simulate an ash pond, the increased ash/water contact time increases the amount of soluble species leached and enhances the approach to steady state. All the design criteria could be met with this filter press arrangement.

Figure 4-1 is a schematic of the ash sluice pilot system. The maximum flow capacity of the system is 190 lpm (50 gpm). The makeup tank (250-gallon capacity) is used to blend ash sluice recycle and makeup water. The flow rates of both streams are measured. The tank is stirred continuously to ensure good blending of the streams. Makeup water is added when the tank level drops below a point corresponding to 150 gallons. The blended sluice water stream is pumped to the mixing tank (100-gallon capacity) where dry fly ash is introduced to form a slurry. The fly ash is added to the mixing tank through a screw feeder which can be adjusted to maintain a constant ash feed rate. The ash is fed from a bin (25-ton capacity) with a gyrating bottom to prevent ash bridging. The ash storage bin is equipped with a blower to allow loading from ash transport trucks. The retention time in the mix tank is approximately 2 minutes at the design flow rate. This corresponds to the average slurry transport (mixing) time from the hydrovactor to the ash pond found at the host power plants.

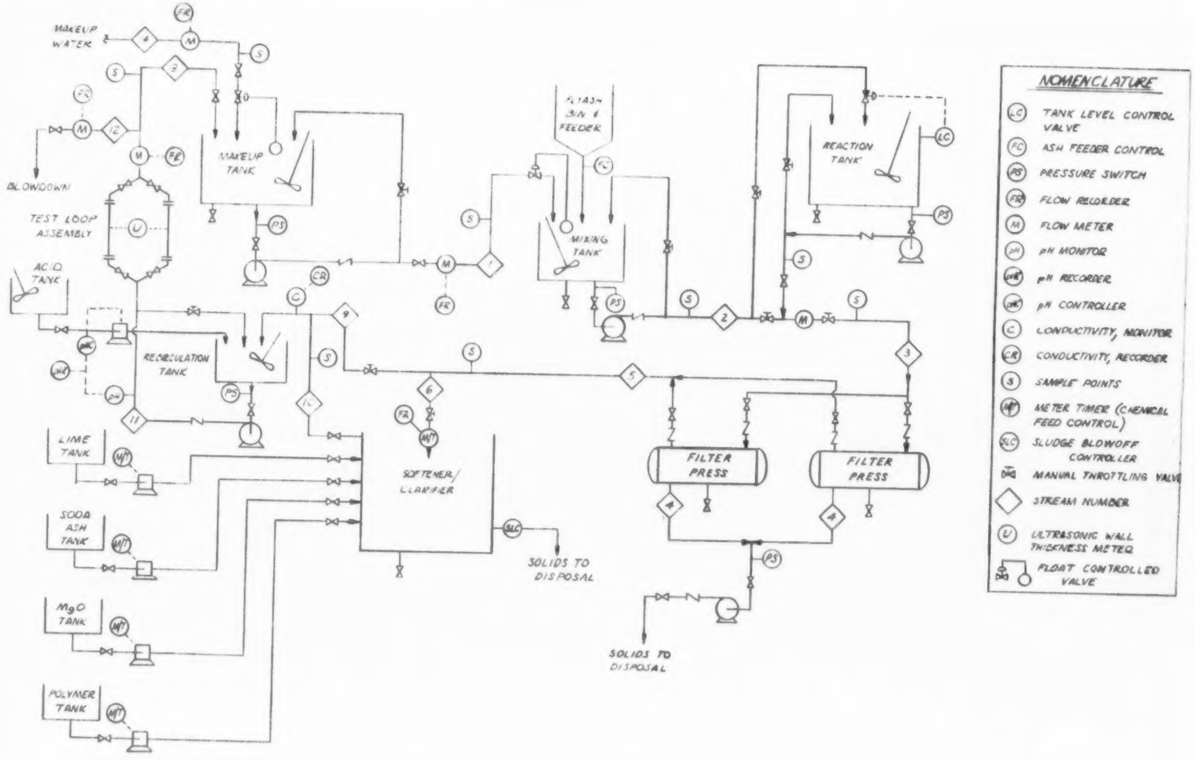

MAKEUP WATER
BLOWDOWN
TEST LOOP ASSEMBLY
ACID TANK
MAKEUP TANK
RECIRCULATION TANK
LIME TANK
SODA ASH TANK
MgO TANK
POLYMER TANK
FLYASH BIN & FEEDER
MIXING TANK
REACTION TANK
SOFTENER/ CLARIFIER
SOLIDS TO DISPOSAL
FILTER PRESS
FILTER PRESS
SOLIDS TO DISPOSAL
NOMENCLATURE
LC TANK LEVEL CONTROL VALVE
FC ASH FEEDER CONTROL
PS PRESSURE SWITCH
FR FLOW RECORDER
M FLOW METER
pH pH MONITOR
pHR pH RECORDER
pHC pH CONTROLLER
C CONDUCTIVITY, MONITOR
CR CONDUCTIVITY, RECORDER
S SAMPLE POINTS
MT METER TIMER (CHEMICAL FEED CONTROL)
SLC SLUDGE BLOWOFF CONTROLLER
MANUAL THROTTLING VALVE
STREAM NUMBER
U ULTRASONIC WALL THICKNESS METER
FLOAT CONTROLLED VALVE

Figure 4-1. Ash Sluice Pilot System Flow Schematic.

The fly ash slurry leaving the mixing tank can be pumped to a reaction/hold tank for additional slurry mixing time or to the filter press for ash removal. The reaction tank (500-gallon capacity) can increase the fly ash/water mixing time up to 10 additional minutes at the design flow rate. The tank mixing time can be varied from 5 to 10 minutes. This reaction/hold tank is used to provide more time for precipitation of scaling species on the suspended ash particles.

The water leaving the mixing tank or reaction tank is pumped to the filter press for ash removal. The filter press (300-gallon volume) filters the ash into a cake on six internal filter leaves. Each filter leaf is covered with a polypropylene fabric. When the holding capacity of the filter press is reached, the spare filter press is placed in service. During cleaning the filter press is pressurized with air to force all water in the filter press back into the system to minimize water losses. Once this blow down is complete the filter is filled with service water. The filter leaves are vibrated and air rolled when the filter is full. The resulting slurry is transferred to the host site ash pond. This fill and drain procedure is repeated until the filter press is clean and ready for service.

The clean filtrate leaving the filter press can enter the recirculation tank or the softener. The recirculation tank (100-gallon capacity) is used to store the filtrate prior to recycle to the makeup tank. Acid can be added to this tank to adjust the pH of the recycle stream. The acid flow is controlled by a pH monitor/controller on the recirculation tank effluent. All or a portion of the filtrate can be sent to the softener. The softener system has four chemical feed systems for addition of lime, soda ash, coagulant, and polymer. The softener (1,000-gallon volume) is a conventional sludge contact unit with a 20-minute retention time at its 175 lpm (45 gpm) design flow rate. The softener is equipped with an automatic sludge blowoff controller. The softener effluent enters the recirculation tank where the pH can be adjusted prior to recycle. Because of budget reductions, the sidestream softener was not tested.

The water leaving the recirculation tank flows through a test loop assembly. The test loop is used to monitor the scaling and corrosion effects in the sluice water recycle line. The test loop assembly consists of two 5.1-cm (nominal 2-in.) diameter schedule 40 stainless steel pipe spools mounted in a parallel configuration. The spools are identical 0.9-m (3.0-ft) lengths, flanged for easy removal. The spools are heat traced and insulated in order to maintain a wall temperature of 40°C (120°F). These test spools are designed to simulate portions of the plant ash sluicing system where elevated temperatures may be encountered. The parallel configuration is valved such that a spool can be easily removed for visual inspection. Water leaving the test loop assembly returns to the makeup tank for reuse in ash sluicing. A portion or all of this stream can leave the system as blowdown. The blowdown stream flow rate is also measured.

The ash sluice pilot unit consists of six portable skid-mounted equipment modules and one control/laboratory building. Each skid is approximately 2.4 by 3 m (8 by 10 ft). The entire test system fits into an area no larger than 6.1 by 12.2 m (20 by 40 ft). The pilot unit can be operated on a 208-, 240-, or 480-volt three-phase power source. The system skids and equipment are interconnected with flexible water hoses and electrical connectors when assembled in the field.

4.2 TESTING APPROACH

Pilot unit field testing focused on determining the technical feasibility of operating a closed-loop recirculating fly ash sluice water system and obtaining steady-state process and analytical data for verification of the ash sluice system computer model. The pilot unit was operated at two host sites (Plant 9677 and Plant 9991). The general approach used at each plant included the following steps:

- gather process and analytical data for the full-scale ash sluice system,
- operate pilot unit at conditions similar to the full-scale system operation, and

- evaluate various water treatment options with the pilot plant to achieve closed-loop operation.

In addition, laboratory batch leaching tests were performed for each ash. The data collected during the testing program were then used to evaluate the ability of the ash sluice system computer program to accurately simulate the pilot system operation. The specific approach was slightly different at the two sites and will be discussed below.

4.2.1 Plant 9677

Pilot unit testing at Plant 9677 investigated the effect of additional ash/water contact time prior to sluicing to reduce the scaling potential of the recirculating water. Three conditions were tested:

- no additional contact time,
- 5 minutes additional contact time, and
- 10 minutes additional contact time.

The original test plan called for tests to include chemical treatment (sulfuric acid solution) and sidestream softening tests to determine the minimum achievable blowdown. However, the test program had to be shortened due to a decrease in project funding. Therefore, the chemical treatment tests and softening tests were deleted from the test program. However, the decreased funding did not substantially alter the testing with no treatment and with additional contact time. Therefore, these tests were conducted over a sufficient period of time to provide steady state data.

The additional contact time was provided by the pilot plant reaction/hold tank. For each test, the system was operated at zero blowdown and a constant slurry of approximately 10 weight percent solids was maintained. The only water loss from the system was the unrecoverable liquid associated with the solids removed in the filter press.

The system was operated for a given set of conditions until steady state was achieved. Steady state was defined to be the point at which the concentrations of certain chemical species were reasonably constant with respect to time. After steady state was achieved, a complete set of characterization samples was taken for analysis.

Based on data from the full-scale system, the pilot unit, and the laboratory studies, the quantity of each species leaching from the ash collected at Plant 9677 was calculated. Also, estimates of the CO_2 transfer (from full-scale plant samples) and solids precipitation occurring in the filter press were made. This information was used as input to the model during the simulation effort. Stream compositions predicted by the model were then compared to the measured compositions to evaluate the ability of the model to accurately simulate pilot unit operation. Further details of the test plan are included in "Field Test Plan for Plant 9677" issued in April 1981 (Appendix F).

4.2.2 Plant 9991

The focus of the pilot unit testing at Plant 9991 was to determine the feasibility of using acid addition as a means of reducing the scaling potential of the recirculating water to enable blowdown rates to be minimized. The effect of the amount of ash in the sluice line on the recirculating water composition was also investigated. The set of six tests performed at Plant 9991 included:

- no treatment, 5 weight percent ash in slurry,
- no treatment, 10 weight percent ash in slurry,
- H_2SO_4 addition, 5 weight percent ash in slurry,
- H_2SO_4 addition, 10 weight percent ash in slurry,
- HCl addition, 5 weight percent ash in slurry, and
- HCl addition, 10 weight percent ash in slurry.

For each set of conditions, the model was used to estimate the minimum blowdown rate without gypsum precipitation. Testing was performed at this blowdown flow rate until steady state operation was achieved. At the conclusion of the test, a complete set of samples was taken for analysis. Further details of the test plan are included in "Field Test Plan for Plant 9991" issued in September 1982 (Appendix G).

The original test plan called for testing using side stream softening to minimize blowdown. However, the test schedule was reduced due to a decrease in funds and this test was omitted. However, the other tests were conducted over a sufficient period of time to achieve steady state operation.

Again, leaching data were determined from the full-scale system, laboratory studies, and pilot plant operation. Estimates of the CO_2 transfer and solids precipitation occurring in the plant pond and filter press, respectively, were used as input to the process model. The actual pilot unit results were then compared to the results predicted by the model, and the model's ability to simulate systems utilizing acid addition was evaluated.

4.3 PLANT DESCRIPTION

Development of a data base for the ash sluice computer model required field testing at a number of power plants. During the course of the program, four potential power plants were considered for field testing with the ash sluice pilot system. Two plants were dropped from the field test plan due to low ash reactivity and funding limitations. Field test programs were undertaken at the remaining two plants, Plant 9677 and Plant 9991. Both these plants produce a fly ash which is highly reactive and results in an alkaline ash sluice water with a high scaling potential for calcium carbonate and/or gypsum. Fly ash produced from western sub-bituminous coal at Plant 9991 contains approximately two times the quantity of soluble calcium as does the fly ash produced from bituminous coal from western Kentucky at Plant 9677. Field testing at these plants provided a broad range of conditions for evaluation of treatment alternatives and the verification of the ash sluice computer process model.

The coal feedstock and operation of the ash sluice system at each of the selected plant sites are quite different. In the following sections, the operation of plant systems pertinent to this program will be briefly described. Detailed comparisons of the plant ash sluice system chemistry, the pilot system, and the computer model predictions will be discussed later in this document.

4.3.1 Plant 9677

Plant 9677 is a 3000 MW electric power generating station consisting of four units. Units 1 and 2 are 700 MW each and Units 3 and 4 are 800 MW each. All units burn bituminous coal from western Kentucky in Bureau of Mines Districts 8 and 9. An analysis of a coal sample taken during a visit to the plant in October 1979 is presented in Table 4-2. The boilers are tangentially-fired and result in about 67 percent of the total ash being fly ash and 33 percent as bottom ash.

Plant 9677 uses wet sluicing and ponding for disposal of both fly ash and bottom ash from all four units. A small portion of fly ash is collected dry and sold locally. Both bottom and fly ash are disposed in a common pond. Other streams which also enter the ash pond include roof and floor drains at a flow rate of about 1500 gpm (5685 lpm) and sewage treatment plant and water treatment wastes at a flow rate of about 66 gpm (250 lpm). A schematic diagram of the ash sluicing system is shown in Figure 4-2.

Plant 9677 has the option of using cooling tower blowdown or ash pond water to sluice bottom and fly ash, as shown in Figure 4-2. Plant makeup water is taken from a nearby river and used for cooling tower makeup. The cooling towers generally operate at 2-3 cycles of concentration. The portion of cooling tower blowdown not used to sluice ash is mixed with the ash pond overflow (after pH adjustment) before being discharged.

Figure 4-2 shows the eight points in the ash handling system at Plant 9677 which were sampled during a visit in October 1979. The analytical

TABLE 4-2. COAL AND ASH ANALYSIS FOR PLANT 9677

Coal Ultimate Analysis

Species	Wt%
Moisture	10.25
Carbon	64.63
Hydrogen	4.45
Nitrogen	1.49
Chlorine	0.05
Sulfur	1.89
Ash	11.07
Oxygen (by difference)	6.17
	100.00

Mineral Analysis of Ash

Species	
SiO_2	51.67
Al_2O_3	23.67
TiO_2	1.17
Fe_2O_3	13.55
CaO	2.35
MgO	1.26
K_2O	2.80
Na_2O	0.54
SrO	0.00
BaO	0.09
SO_3	0.87

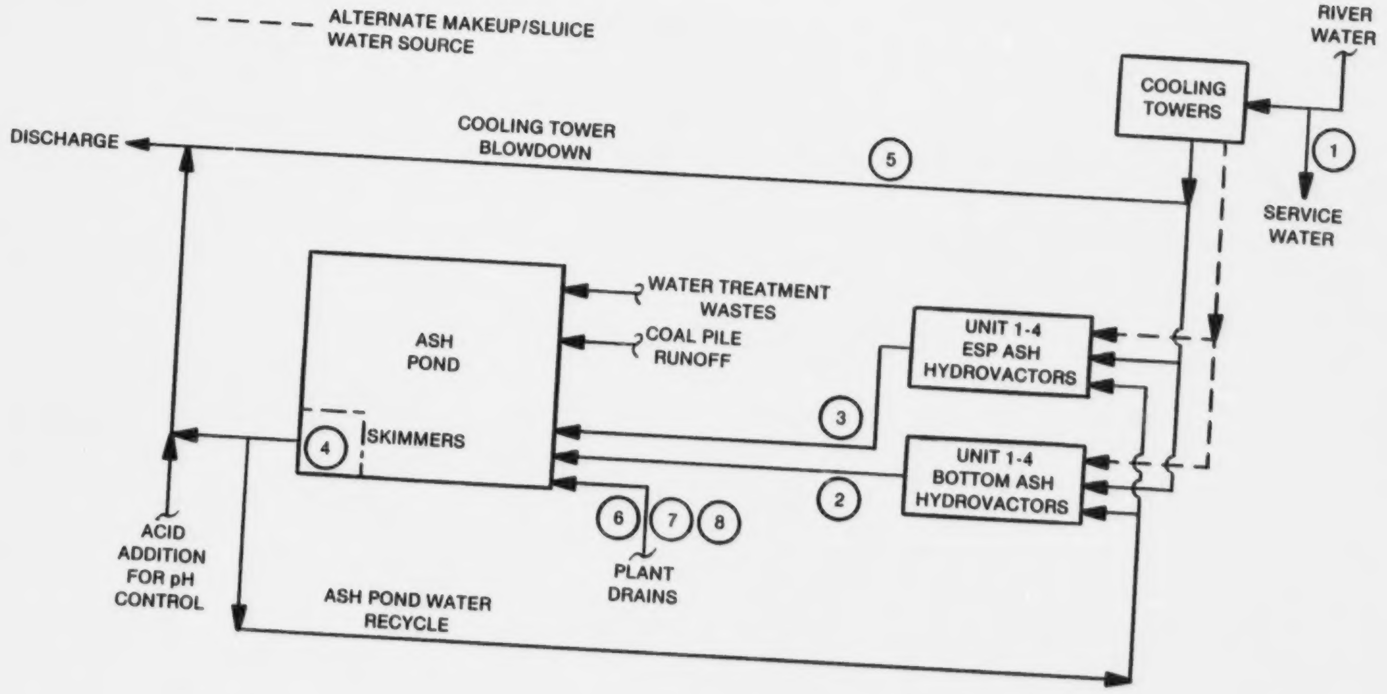

ALTERNATE MAKEUP/SLUICE WATER SOURCE
RIVER WATER
COOLING TOWERS
1
SERVICE WATER
DISCHARGE
COOLING TOWER BLOWDOWN
5
ASH POND
WATER TREATMENT WASTES
COAL PILE RUNOFF
UNIT 1-4 ESP ASH HYDROVACTORS
3
SKIMMERS
4
UNIT 1-4 BOTTOM ASH HYDROVACTORS
2
6
7
8
PLANT DRAINS
ACID ADDITION FOR pH CONTROL
ASH POND WATER RECYCLE
70A3179

Figure 4-2. Flow Diagram of Ash Sluice System at Plant 9677.

results from those samples are presented in Table 4-3. This table shows the major species concentrations (Ca, Mg, Na, K, Si, SO_4, Cl, and total carbonate) as well as the measured pH, temperature, and suspended solids content for slurry streams. The three miscellaneous plant drain streams shown in the tables were sampled as they entered the ash pond and are floor and roof drains from various parts of the plant. The fly ash and bottom ash slurries were sampled from Unit 4. The plant has encountered some scaling problems in the ash sluice line before pH control was installed. However, scaling has been avoided since the plant began controlling pH.

The total ash production at Plant 9677 under full load conditions is about 72,000 kg/hr (79 tons/hr) fly ash and 35,500 kg/hr (39 tons/hr) bottom ash for all four units (based on 10 percent ash in the coal). The average sluice rate for fly ash is 50,000 lpm (13,200 gpm) which corresponds to about 4 percent solids in the fly ash slurry. Fly ash is typically sluiced for about 2-1/2 hours every 4 hours. The average daily sluice rate for bottom ash is 44,000 lpm (11,600 gpm) which corresponds to about 2.7 weight percent solids in the bottom ash slurry. The instantaneous level of solids in the ash slurries can vary significantly, as shown by the sample analyses in Table 4-3. During a sluicing operation, the solids content of the slurry generally starts at a high value and decreases as ash is removed from a particular hopper or set of hoppers.

At Plant 9677, the bottom ash is conveyed from the boilers to the ash pond through 10-in. diameter pipes. One pipe is used for each boiler. The distance from the boilers to the ash pond entry point varies from 490 m (1600 ft) for Unit 1 to 690 m (2300 ft.) for Unit 4. The fly ash from Units 1 and 2 is collected by electrostatic precipitators and slurried to the ash pond in 10-in. diameter pipes (one per boiler). The fly ash from Units 3 and 4 is also collected by electrostatic precipitators and sluiced in 10-in. diameter pipes to the ash pond. Two pipes for each of Units 3 and 4 are used to sluice fly ash.

TABLE 4-3. ASH SYSTEM SAMPLE ANALYSES RESULTS FOR PLANT 9677

Sample Point	Date	Ca	Mg	Na	K	Si	SO_4	Cℓ	CO_3	pH	Temperature °C	Wt% Solids	Gypsum Relative Saturation
		mg/l											
Service Water	10/29 p.m.	11.8	2.1	3.7	1.7	5.0	8.6	3.2	28.8	7.2	19	-	.001
	10/30 a.m.	8.5	1.9	2.8	1.4	4.8			29.4	6.9	17	-	
	10/31 a.m.	8.2	1.9	2.7	1.3	4.9			33.6	7.0	17	-	
Bottom Ash Slurry	10/29 p.m.	22.9	3.0	4.6	2.1	7.9	16.3	5.0	60.6	7.2	28	0.65	.002
	10/30 a.m.	43.4	2.9	4.8	2.6	7.7	78.7	4.6	60.0	6.2	36	2.60	.017
	10/30 p.m.	38.6	3.0	4.0	2.4	8.5	56.6	5.3	62.4	6.5	37	0.44	.012
	10/31 a.m.	64.5	2.8	15.9	5.5	6.0	180.0	5.7	55.2	4.0	37	7.94	.046
Fly Ash Slurry	10/29 a.m.	322.	7.1	10.9	19.1	3.3	484.0	5.7	19.2	6.3	27	6.20	.298
	10/29 p.m.	257.	5.1	11.8	20.9	3.0	396.0	5.0	26.4	9.8	29	7.78	.218
	10/30 a.m.	297.	7.8	12.7	22.5	9.7	601.0	6.0	23.4	4.7	26	6.80	.334
	10/30 p.m.	163.	4.3	6.4	10.5	4.6	223.0	6.0	38.4	9.6	29	3.15	.103
	10/31 a.m.	97.7	3.7	18.8	8.0	10.3	227.0	6.0	28.2	5.6	18	0.37	.078
Ash Pond Water	10/29 a.m.	89.2	3.2	18.6	6.3	6.0	182.0	6.4	21.6	9.7	18	-	.059
	10/29 p.m.	85.7	3.3	21.2	6.9	5.6			18.0	9.6	18	-	.058
	10/30 a.m.	52.6	3.2	24.6	8.7	4.5			21.6	9.6	17	-	.039
	10/30 p.m.	55.0	3.3	24.7	8.8	4.9			19.8	9.5	18	-	.040
	10/31 p.m.	57.7	3.2	23.2	7.8	4.7			25.8	9.5	18	-	.042
Circulating Cooling Water	10/29 p.m.	16.4	3.2	3.1	2.2	7.3	10.6	5.0	60.0	8.2	25	-	.001
	10/30 a.m.	18.7	3.3	3.3	2.3	7.8			66.6	8.2	27	-	.001
	10/31 a.m.	24.8	4.0	4.9	3.1	10.0			85.2	8.4	28	-	.002
Miscellaneous Plant Drain 1	10/29 a.m.	17.6	1.1	46.9	2.5	3.5	66.2	5.3	43.2	9.6	22	0.24	.006
	10/29 p.m.	13.1	1.5	23.8	2.2	3.6			39.0	9.5	22	0.80	.005
Miscellaneous Plant Drain 2	10/30 a.m.	15.2	3.0	2.8	1.6	4.3	24.0	3.9	33.6	6.7	24	0.08	.002
	10/30 p.m.	14.3	2.3	4.0	1.7	4.5			42.0	8.2	21	0.21	.002
Miscellaneous Plant Drain 3	10/31 a.m.	16.0	2.5	4.5	2.2	7.2	14.4	5.0	52.2	7.6	26	-	.002

The plant floor and roof drains are collected and enter the ash pond at the same point as the fly ash and bottom ash. The ash pond has a surface area of about 1.1 million m^2 with an average depth of 14 m. As shown in Figure 4-2, the pond overflow pH is adjusted with sulfuric acid prior to mixing with cooling tower blowdown for final discharge.

4.3.2 Plant 9991

Plant 9991 is a nominal 1000 MW electric generating station consisting of two identical 500 MW units. All units burn low sulfur western subbituminous coal from eastern Utah and western Colorado. An analysis of the average design coal is presented in Table 4-4. The coal is washed prior to shipment, resulting in an ash content of approximately 10 weight percent. After combustion, 85 percent of the ash is produced as fly ash with the remaining 15 percent as bottom ash.

Plant 9991 uses wet sluicing and ponding as the primary means for disposal of both fly ash and bottom ash from both units. A portion of fly ash is collected dry and sold locally. Fly ash is transported from the electrostatic precipitators to a hydrovactor, where it is mixed with recycled pond water. Each generating unit has two hydrovactors but normally operates with only one in service. The fly ash is sluiced from the hydrovactor to a fly ash settling pond on a continuous basis. Bottom ash is sluiced to a separate pond on a once-per-day basis. Decant from the fly ash pond overflows to the bottom ash pond from which it is recycled as shown in Figure 4-3. The recycled water is used to supply water to both bottom ash hoppers and fly ash hydrovactors. The overall system is operated in a closed-loop mode. The only losses from the system are through evaporation and water occluded with the ash. Makeup water enters the system in the fly ash settling pond. The only sources of makeup water for this system are coal pile runoff and treated wastewaters from the plant which include floor drains and demineralizer regeneration wastes. Service water can also be used as makeup to the ash sluice system. However, service water makeup has not been used for this purpose since the original plant startup.

TABLE 4-4. COAL AND ASH ANALYSIS FOR PLANT 9991.

Coal Ultimate Analysis

Species	Wt%
Moisture	8.5
Carbon	61.1
Hydrogen	4.7
Nitrogen	1.2
Sulfur	3.7
Ash	14.0
Oxygen (by difference)	6.8
	100.0

Mineral Analysis of Ash

Species	Wt%
SiO_2	51.03
Al_2O_3	35.70
TiO_2	1.28
F_2O_3	2.98
CaO	4.84
MgO	1.23
K_2O	0.38
Na_2O	0.98
SO_3	1.00
P_2O_5	0.20
SrO	0.08
BaO	0.23
Mn_3O_4	0.01
Undetermined	0.06
	100.00

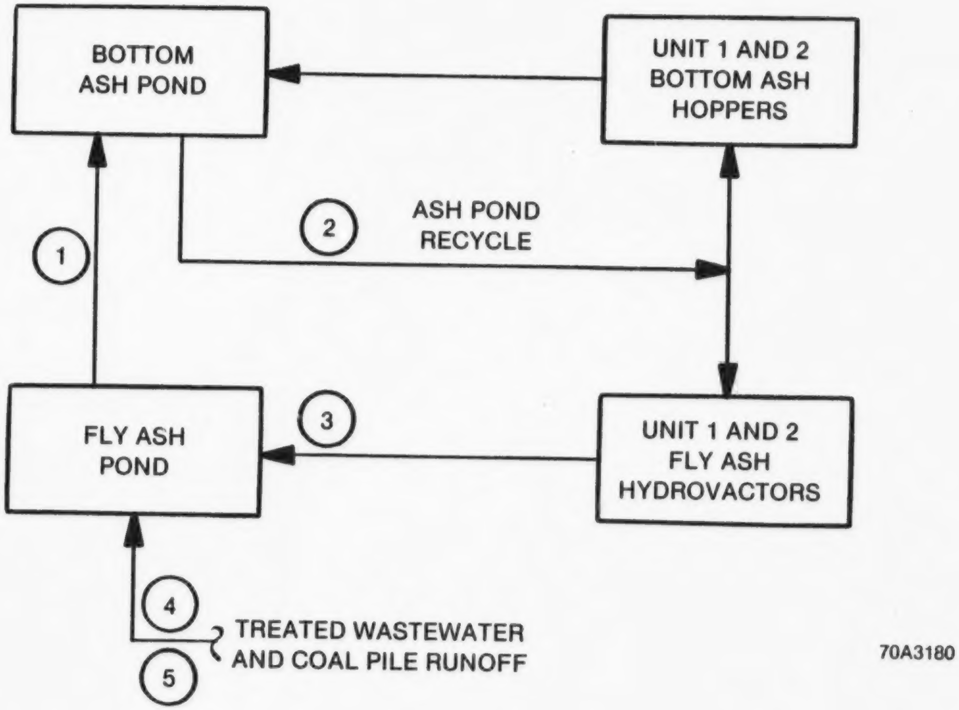

BOTTOM ASH POND
UNIT 1 AND 2 BOTTOM ASH HOPPERS
①
②
ASH POND RECYCLE
FLY ASH POND
③
UNIT 1 AND 2 FLY ASH HYDROVACTORS
④
⑤
TREATED WASTEWATER AND COAL PILE RUNOFF
70A3180

Figure 4-3. Flow Diagram of Ash Sluice System at Plant 9991.

Figure 4-3 shows the five points in the ash handling system at Plant 9991 which were sampled during the plant visit in August 1982. The analytical results for these samples are included in Table 4-5. The table presents the major species (Ca, Mg, Na, K, SiO_2, SO_4, Cl and total carbonate) as well as the measured pH, temperature, and suspended solids content for slurry streams. An analysis of the service water was also performed, since the stream would be used for flushing of fly ash sludge from the filter presses in the pilot system and represented a potential source of contamination. A sample of the bottom ash was collected by plant personnel and sent to Radian after the plant visit. Plant 9991 has experienced scaling of ash water recycle pump screens. However, the scaling has not been severe enough to cause a major problem in the operation of the plant. The plant is relatively new and the ash sluice water had not concentrated significantly at the time of the field tests with the pilot system. Scaling may become a problem after the plant has operated for several years.

The total ash production at Plant 9991 under full-load conditions is about 32,700 kg/hr (38 tons/hr) fly ash and 5800 kg/hr (6.4 tons/hr) bottom ash for both units (based on 10 percent ash in the coal). The average daily sluice rate for fly ash is 11,700 lpm (3080 gpm), which corresponds to about 5 weight percent solids in the fly ash slurry. Fly ash is sluiced continuously. The daily sluice rate for bottom ash is 11,400 lpm (300 gpm) which corresponds to about 17 weight percent solids in the bottom ash slurry. Bottom ash is sluiced once per day for approximately one hour. The instantaneous level of solids in the ash slurries can vary significantly. During a sluicing operation, the solids content of the slurry generally starts at a high value and decreases as ash is removed from a particular hopper or set of hoppers.

At Plant 9991, the bottom ash is conveyed from the boilers to the ash pond through 25-cm (10-in.) diameter pipes. One pipe is used for each boiler, and these lines are approximately 150 m (500 ft) long. The fly ash is collected by electrostatic precipitators and slurried to the ash pond in 35-cm (14-in.) diameter pipes (one per boiler). These sluice lines are approximately 500-m (1600-ft) long. During the field test, only ash from the upper precipitator of Unit 1 was available.

TABLE 4-5. ASH SYSTEM SAMPLE ANALYSES RESULTS FOR PLANT 9991

Sample Number	Sample Point	Date	Ca	Mg	Na	K	SiO_2	SO_4	Cl	CO_3	pH	Temperature °C	Wt% Slurry	Saturation of $CaCO_3$
			mg/l											
1	Fly Ash Pond Crossover to Bottom Ash Pond	8/12/82	220	2.3	80.0	3.1	13.7	420.	37.0	12.8	10.4	28		17.3
2	Ash Sluice Return Water	8/12/82	131	2.4	77.0	3.4	14.1	285.	38.0	13.6	10.4	31		17.5
3	Fly Ash Slurry Water	8/12/82	450	7.9	110.	5.3	11.6	530.	51.0	13.8	11.3	31	3.6	26.6
4	Treated Wastewater	8/12/82	67.0	1.1	65.0	1.4	6.4	194.	38.0	81.0	8.1	38		2.8
5	Coal Pile Runoff	8/12/82	86.0	4.5	56.0	1.8	6.6	280.	31.0	68.5	8.9	32		11.0
6	Service Water	8/12/82	12.2	0.6	170	0.9	16.5	43	56	450	8.9	34		11.1

The plant coal pile runoff and treated wastewater are collected and enter the fly ash pond at the same point as the fly ash slurry. The makeup water to the system is a blend of these two streams which will vary, depending on plant operations. Treated wastewaters consist of plant drainage and demineralizer regeneration wastes which have been neutralized and clarified prior to entering the ash system.

4.4 PILOT UNIT TESTING AT PLANT 9677

The approach used at Plant 9677 to meet the program objectives included: 1) characterization of the full-scale ash sluice system, 2) laboratory leaching studies, and 3) pilot unit testing. The work at Plant 9677 focused on determining the effect of increased ash/water contact time on the potential for scaling in the recirculating line and evaluating the ability of the model to accurately simulate the pilot unit operation. In addition, data collected during the testing were used to determine the adequacy of laboratory leaching data for use as input to the ash sluice model.

During testing at Plant 9677, some operating problems with the filter presses were encountered which required ash to be sluiced on an intermittent basis. However, it is also common practice in full-scale facilities to sluice ash periodically. During periods when ash sluicing was interrupted, the ash water was recirculated and the pH and conductivity remained constant. Therefore, the intermittent operation of the pilot unit due to the filter operating problems did not appear to affect the test results.

The results of testing at Plant 9677 indicate that:

- The quantities of the major species leaching from the ash for the full-scale and pilot systems can adequately be estimated from laboratory batch leaching data for use as input to the process model.
- For a full-scale system sluicing a similar fly ash, the incorporation of a reaction/hold tank to provide additional ash/water mixing time up to 10 minutes would not significantly reduce the potential for scale formation in the recirculating water stream.

In the following subsections, the results of testing at Plant 9677 will be discussed. First, the fly ash leaching data are presented, followed by a presentation and discussion of the pilot unit testing. Next, the pilot unit results are compared to the ash sluice model's predictions to evaluate the ability of the model to simulate the pilot unit operation.

4.4.1 Fly Ash Leaching

The quantity of soluble species leaching from the ash (leachability) is an important input parameter for the ash sluice computer model. In the past, a laboratory procedure has been used to determine the leachability for use as input to the model. However, prior to this program it was unknown if the values calculated from the laboratory procedure reflected the actual quantities leached during sluicing in a full-scale system. For this reason, a comparison of the leachability results for the full-scale system and pilot unit were compared to the laboratory leachability results.

The quantity of each major species (calcium, magnesium, sodium, potassium, chloride, sulfate) leaching from the ash was calculated for each set of data by the following equation:

$$QL_S = \left(\frac{[S]_{slurry} - [S]_{sluice}}{10^6}\right)\left(\frac{1 - X_{ash}}{X_{ash}}\right) 1000 \qquad (4\text{-}1)$$

where:

QL_S = the quantity of species S leached per unit of ash (mg/g),

$[S]_{slurry}$ = the concentration of species S in the slurry liquid (ppm),

$[S]_{sluice}$ = the concentration of species S in the sluice water before ash addition (ppm), and

X_{ash} = the weight fraction of ash in the slurry.

During leaching of alkaline ash, the increased concentration of calcium and the high resulting pH may result in the precipitation of calcium carbonate. If sulfate concentrations are high enough, precipitation of gypsum ($CaSO_4 \cdot 2H_2O$) may occur. And, at very high pH values (>10.0), precipitation of $Mg(OH)_2$ may also occur. Precipitation of any of these species will affect the calculated leachability and must be considered.

In the cases where calcium carbonate precipitation was indicated by supersaturated conditions, calculated QL_{Ca} value was increased by the equivalent change in the carbonate concentration of the sluice and slurry water. If gypsum precipitation was indicated, a similar approach could not be used since sulfate was also leaching. In these cases, the assumption was made that the quantity of sulfate leaching from the ash was equivalent to the quantity leaching during the laboratory procedure when precipitation of gypsum was not indicated. The difference in the calculated quantity of sulfate leaching from the ash and the expected value was attributed to the precipitation of gypsum. The calcium leachability was then increased by an equivalent amount.

4.4.1.1 Laboratory Leaching Procedure--

In conducting the laboratory batch leaching tests, a known quantity of fly ash was mixed with a known volume of deionized water and agitated until a constant pH was achieved. At the completion of the test, the composition of the leachate was determined, and the quantity of soluble species leached from the ash was calculated based on the amount of ash present in the slurry. This procedure was used for screening studies of both Plant 9677 and Plant 9991. During the testing at Plant 9991 makeup water was used in place of deionized water to provide more realistic leaching data.

Since the quantity of carbonate introduced with the deionized water was minimal and the beakers were covered to prevent transfer of CO_2 from the atmosphere, the precipitation of calcium carbonate was assumed to be insignificant for the laboratory tests. Also, the relative saturation of gypsum did not exceed 1.0 during the laboratory testing so the precipitation of gypsum would not be expected.

Figure 4-4 illustrates the pH versus time curve typically seen during the laboratory leaching with Plant 9677 fly ash. An interesting aspect of the curve is the decrease in pH occurring in the first minute of ash/water contact, followed by a rapid rise to the equilibrium pH. This was common to all the pH versus time plots. The decrease in pH probably results from the initial leaching of acidic sulfate from the surface of the fly ash. The preferential deposition of sulfate on the surface of the fly ash is thought to occur when the alkaline ash is exposed to elevated levels of sulfur dioxide (SO_2) in the flue gas where SO_2 adsorbs to the ash surface. When this ash is contacted with water, the sulfate dissolves first resulting in a decrease in pH. The rapid rise in the leachate pH results from the dissolution of alkaline species (MgO, CaO, Na_2O, etc.) in the ash. Based on the measured pH the major portion of the soluble species are leached in the first 5 to 10 minutes of ash/water contact.

4.4.1.2 Data Collected During Pilot Unit Testing—

Leaching data were collected from three sources during the field test program: 1) laboratory batch tests, 2) the full-scale system, and 3) the pilot unit. The results of the leaching studies are summarized in Table 4-6.

Both the average values and range of calculated values are presented. Variations in the calculated leachabilities can be attributed to two factors. First, there is some analytical error associated with the values used to calculate the quantity of a species leached from the ash. Second, it is expected that the composition of the coal being burned fluctuates, resulting in changes in the ash and hence the ash leachability. An error propagation analysis was performed to estimate the error associated with the analytical measurements. The results of this analysis indicate that for a 95 percent confidence limit in the calculated leachabilities, the coefficient of variation for the analytical measurements was approximately ±20 percent. The fact that in many cases the range of values exceeds this limit indicates that changes in the ash composition may also contribute to the variation in the leachability data.

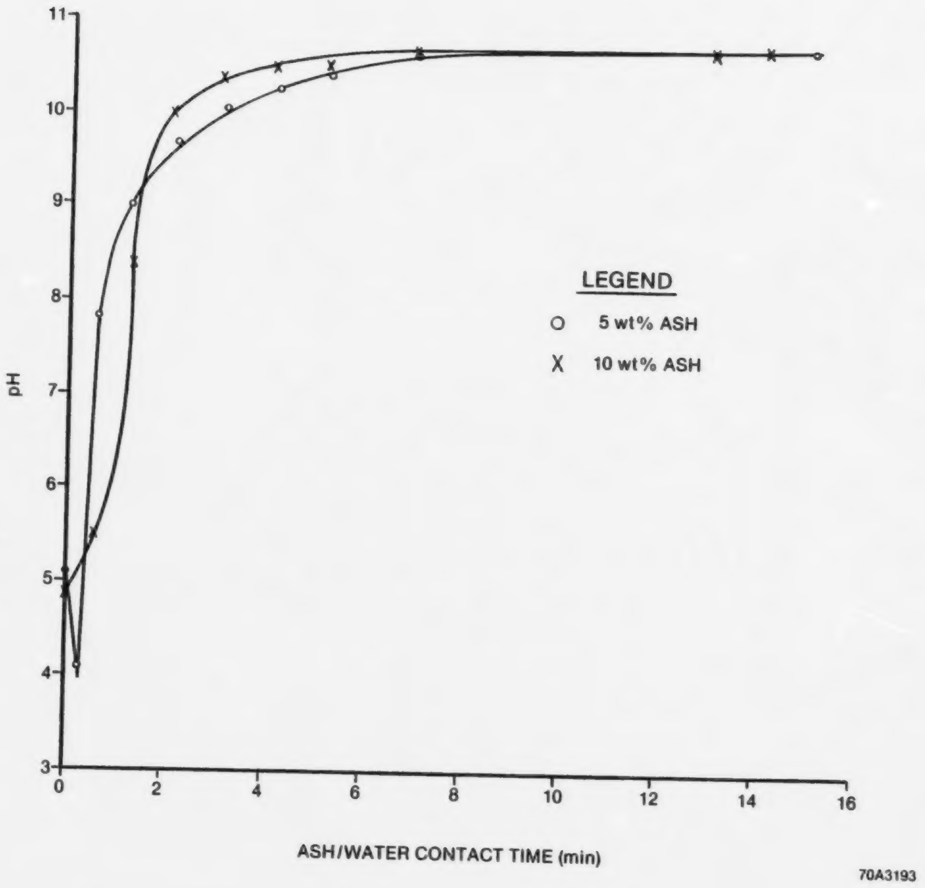


Figure 4-4. pH vs. Ash/Water Contact Time for Batch Fly Ash Lab Studies.

TABLE 4-6. SUMMARY OF ASH LEACHING DATA--PLANT 9677

	Quantity Leached, mg/g ash							Relative Saturation	
Data Source	Calcium	Magnesium	Sodium	Potassium	Chloride	Sulfate	Slurry pH	Calcium Carbonate	Gypsum
Field Laboratory[a]									
- average	4.2	0.02	0.12	0.17	0.03	6.5		29	0.3
- range	3.6-5.3	0.01-0.04	0.10-0.16	0.13-0.20	0.00-0.08	4.0-10.1	10.0-11.0	19-45	0.1-0.5
Full-Scale System									
- average	4.1	0.05	0.11	0.25	0.02	6.6		a	0.2
- range	3.2-5.0	0.02-0.07	0.10-0.13	0.22-0.27	0.00-0.03	4.6-8.1	4.7-9.8	0.01-30.8	0.1-0.3
Pilot Unit									
- average	3.3	0.03	0.09	0.18	b	6.5[c]		>100	2.2
- range	2.9-3.8	0.01-0.05	0.02-0.20	0.06-0.35			10.2-10.5		1.9-2.5

[a] Average not reported due to variations in pH.

[b] No leaching was measures.

[c] Could not be measured due to precipitation of gypsum and was assumed to be the same as the laboratory value.

Also shown in Table 4-6 are the relative saturation values calculated by the equilibrium model for the leachate. These values were used to determine if the potential for precipitation of either calcium carbonate or gypsum existed during leaching. In each case, a potential for precipitation of calcium carbonate was present. The quantity of calcium carbonate actually precipitated was calculated based on the change in the carbonate concentration. The potential for gypsum precipitation existed only during the pilot unit tests. Results of pilot unit testing also indicate that precipitation of gypsum occurred in the system based on the low apparent leachability (1.6 mg SO_4/g ash). To estimate the quantity of calcium precipitated with the gypsum, it was assumed that the sulfate leachability in the pilot unit was equivalent to the calculated leachability during the laboratory batch testing. The difference between this value (6.5 mg SO_4/g ash) and the apparent leachability was assumed to have precipitated as gypsum.

As shown in Table 4-6, the results of laboratory leaching for Ca, Mg, Na, K, Cl, and SO_4 agree well with both the full-scale and pilot unit leaching data. One difference is the lower calcium leachability calculated for the pilot unit. This difference may not represent an actual difference in the quantity of calcium leached, but could indicate that additional precipitation of calcium in the pilot unit occurred but was not accounted for. This could be caused by the addition of carbonate from either the atmosphere or carbonate leaching (it was assumed that no carbonate leached from the ash) which precipitated as calcium carbonate, or the actual sulfate leachability was slightly higher than assumed. The results of the leaching tests indicate that using the laboratory leachability data as input to the model is a reasonable approach to modeling a fly ash sluice system.

4.4.2 Results of Pilot Unit Tests

The pilot unit test program was conducted in May of 1981 and consisted of three tests. The primary objective of the field program was to evaluate the technical feasibility of operating a closed-loop recirculating fly ash sluice system. The pilot unit was operated at a minimum blowdown (maximum recycle) with two pilot unit configurations:

- no water treatment, and
- incorporation of a reaction/hold tank to allow additional ash/water contact time prior to sluicing.

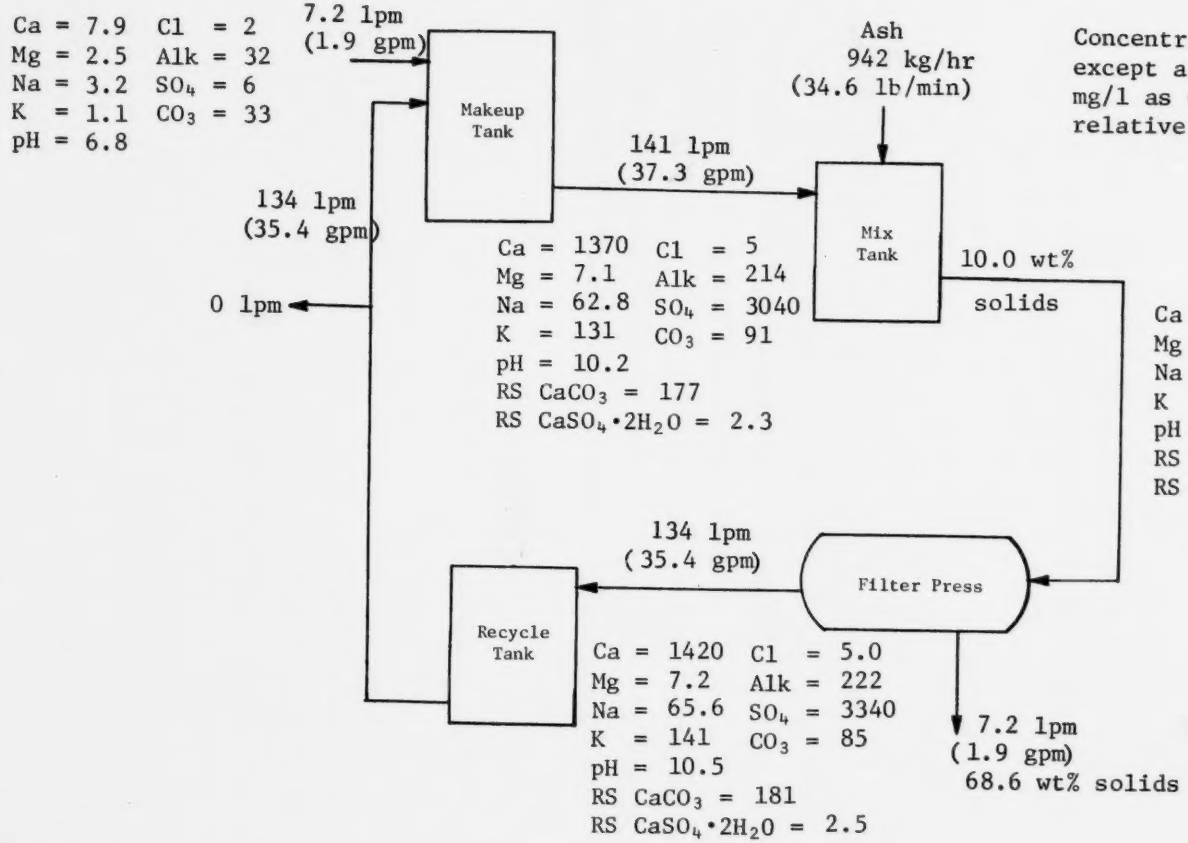
The purpose of this testing was to determine the effect of additional ash water/contact time on the potential for precipitation in the recirculating water stream. The increased ash/water contact would encourage precipitation of supersaturated species on the ash; whereas in a pond the solids would settle and the surface area available for precipitation would be minimized.

Three tests were completed at reaction tank residence times of 0, 5, and 10 minutes. The slurry in the reaction tank was well mixed. The level in the tank was adjusted to change the residence time. All of the pilot unit tests at Plant 9677 were conducted at zero blowdown. The results of the tests are discussed below.

4.4.2.1 Baseline Pilot Tests - No Treatment--

The first test was conducted without the reaction tank to serve as a base case. The pilot unit was operated at zero blowdown and 10 weight percent solids in the sluice line until steady-state operation was achieved. The pilot unit was considered to be operating at steady-state when the concentration of calcium and sodium at key locations showed no significant variation over three 4-hour sampling periods. At this time, samples of all the process streams were collected, filtered, and preserved. The samples were then analyzed to determine the liquid phase composition and weight percent solids. The liquid phase compositions were input to the equilibrium model to determine the potential for precipitation in the stream.

The results of Test 1 are summarized in Figure 4-5. The carbonate concentrations were not measured directly, but were calculated from the measured alkalinity values. As would be expected, the concentration of all the major species increased across the mix tank except chloride and carbonate. The chloride concentration remained constant indicating very little or no leaching of chloride, which is consistent with both the laboratory and full-scale data.


Ca = 7.9 Cl = 2
Mg = 2.5 Alk = 32
Na = 3.2 SO_4 = 6
K = 1.1 CO_3 = 33
pH = 6.8
7.2 lpm
(1.9 gpm)
Makeup Tank
134 lpm
(35.4 gpm)
0 lpm
141 lpm
(37.3 gpm)
Ca = 1370 Cl = 5
Mg = 7.1 Alk = 214
Na = 62.8 SO_4 = 3040
K = 131 CO_3 = 91
pH = 10.2
RS $CaCO_3$ = 177
RS $CaSO_4 \cdot 2H_2O$ = 2.3
Ash
942 kg/hr
(34.6 lb/min)
Mix Tank
10.0 wt% solids
Ca = 1440 Cl = 5
Mg = 8.5 Alk = 89.5
Na = 71.2 SO_4 = 3640
K = 144 CO_3 = 49
pH = 9.4
RS $CaCO_3$ = 58.8
RS $CaSO_4 \cdot 2H_2O$ = 2.7
Filter Press
134 lpm
(35.4 gpm)
Recycle Tank
Ca = 1420 Cl = 5.0
Mg = 7.2 Alk = 222
Na = 65.6 SO_4 = 3340
K = 141 CO_3 = 85
pH = 10.5
RS $CaCO_3$ = 181
RS $CaSO_4 \cdot 2H_2O$ = 2.5
7.2 lpm
(1.9 gpm)
68.6 wt% solids

Concentrations in mg/l as ion except alkalinity which is in mg/l as $CaCO_3$. RS stands for relative saturation.

Figure 4-5. Summary of Pilot Unit Data from Test 1--Plant 9677.

The decrease in carbonate suggests that some calcium carbonate precipitated in the mix tank (residence time approximately 3 minutes). The low apparent sulfate leachability (2.9 versus 6.5 mg SO_4/g ash for laboratory tests) across the mix tank suggests that some precipitation of gypsum also occurred in the mix tank. The high relative saturation (RS) values calculated by the equilibrium model indicate that the potential for precipitation of both calcium carbonate and gypsum existed in the mix tank.

The decrease in sulfate concentration between the mix tank effluent and the recycle tank effluent suggests that some additional precipitation of gypsum occurred in either the sluice line, the filter press, or the recycle tank. The calcium, however, did not decrease an equivalent amount. This could be accounted for by additional leaching of calcium from the ash. Additional leaching would be expected based on the laboratory leaching tests which indicated complete leaching requires approximately 10 minutes (Figure 4-4).

The carbonate concentration increased between the mix tank effluent and the recycle tank effluent. There are two potential sources of carbonate: 1) CO_2 transfer from the atmosphere, and 2) leaching of carbonate from the ash. Although both of these explanations are possible, due to the potential analytical error in carbonate numbers (since carbonate was not measured directly) and the relatively low values, the change in carbonate was not felt to be significant in evaluating the results.

A value required as input for the ash sluice system computer model is the approach to solid-liquid equilibrium achieved in the ash settling pond. Experience indicates that some precipitation of supersaturated species occurs in an ash pond. However, from the calculated relative saturation values it was determined that solid-liquid equilibrium was not achieved. To quantify precipitation in the ash sluice system, the approach to equilibrium was calculated using Equation 3-4.

The results of Test 1 indicate that both gypsum and calcium carbonate precipitated in the system. However, the majority of this precipitation occurred in the presence of the fly ash (in the mix tank, sluice line and filter press), which may not result in scaling. The high relative saturation values for the recycle tank effluent indicate that the potential for both calcium carbonate and gypsum precipitation existed in the recirculating stream. Although positive identification of neither calcium carbonate nor gypsum scale was made during the test, operation at similar conditions for extended periods of time would probably result in scaling in the recirculating water line.

4.4.2.2 Reaction/Hold Tank (5-Minute Residence Time)—

During Test 2, the slurry from the mix tank was pumped to a reaction/hold tank. The level in the reaction tank was maintained at a point to provide a 5-minute residence time. The reaction tank contents were agitated. The results of Test 2 are summarized in Figure 4-6.

Again, increases in the concentrations of the major species except for chloride and carbonate were measured across the mix tank. Precipitation of both gypsum and the calcium carbonate in the mix tank was indicated from the chemical data and implied based on the high relative saturation values calculated by the equilibrium model.

As shown, the composition changed very little across the reaction tank. The differences in the calcium, sulfate, and carbonate concentrations were within analytical error (±5 percent). This suggests that little if any precipitation actually occurred in the mix tank.

It is interesting to note that between the reaction tank effluent and the recycle tank effluent a considerable quantity of gypsum precipitation occurred. It is assumed that most of this precipitation occurred in the filter press where additional residence was provided. It appears, however, that the extent of precipitation was greater in the filter press than in the reaction/hold tank. The change in the calcium value is slightly lower than would be expected based on the change in sulfate suggesting some additional leaching of calcium may have occurred in the filter press. The increase in the carbonate concentration across the reaction tank again suggests a contribution of carbonate either from the ash or through CO_2 transfer from the atmosphere. The approach to solid-liquid equilibrium for gypsum calculated for Test 2 was 44 percent.

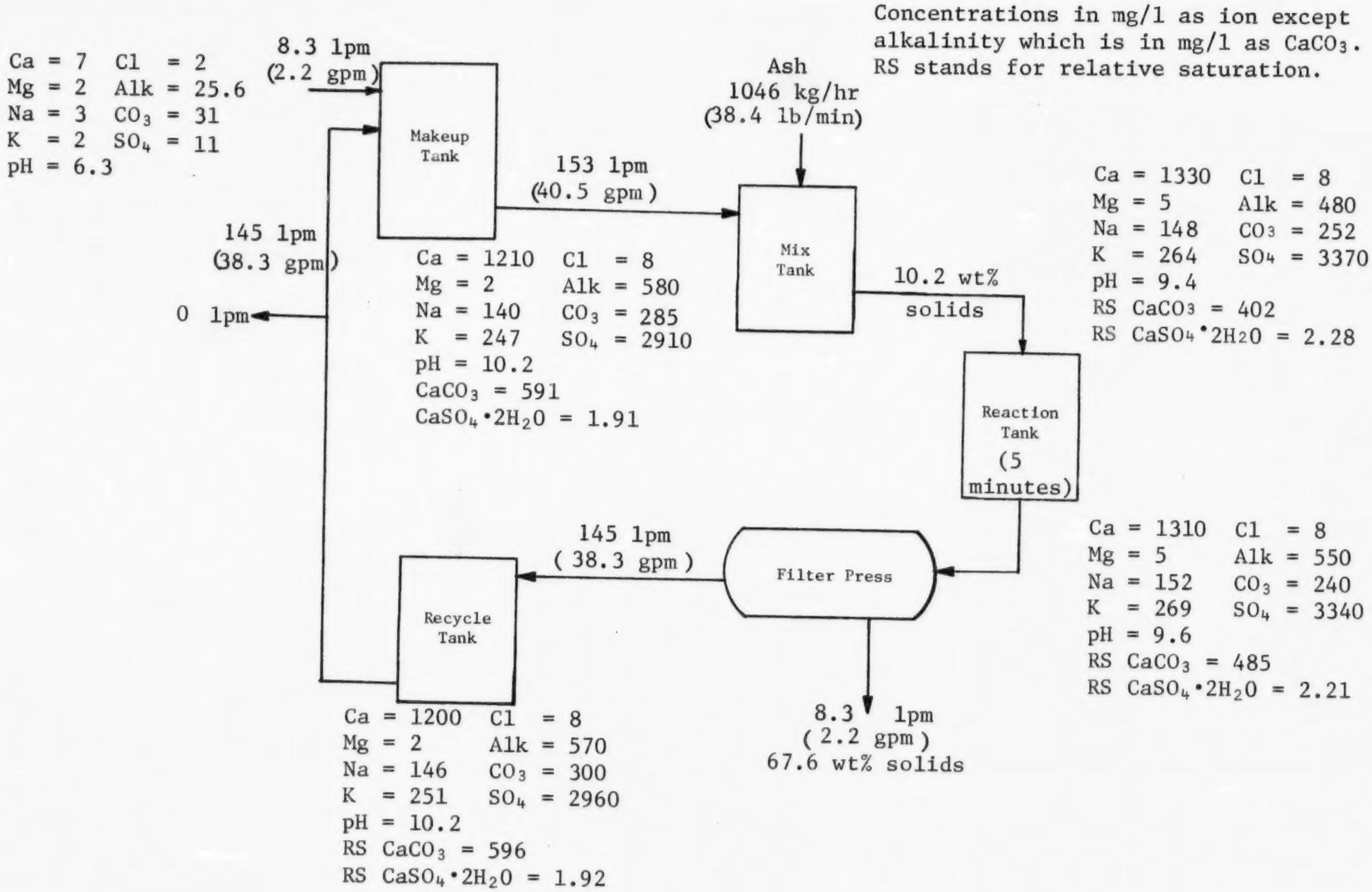

Concentrations in mg/l as ion except alkalinity which is in mg/l as $CaCO_3$. RS stands for relative saturation.
Ca = 7 Cl = 2
Mg = 2 Alk = 25.6
Na = 3 CO_3 = 31
K = 2 SO_4 = 11
pH = 6.3
8.3 lpm (2.2 gpm)
Makeup Tank
145 lpm (38.3 gpm)
0 lpm
153 lpm (40.5 gpm)
Ca = 1210 Cl = 8
Mg = 2 Alk = 580
Na = 140 CO_3 = 285
K = 247 SO_4 = 2910
pH = 10.2
$CaCO_3$ = 591
$CaSO_4 \cdot 2H_2O$ = 1.91
Ash 1046 kg/hr (38.4 lb/min)
Mix Tank
10.2 wt% solids
Ca = 1330 Cl = 8
Mg = 5 Alk = 480
Na = 148 CO_3 = 252
K = 264 SO_4 = 3370
pH = 9.4
RS $CaCO_3$ = 402
RS $CaSO_4 \cdot 2H_2O$ = 2.28
Reaction Tank (5 minutes)
Ca = 1310 Cl = 8
Mg = 5 Alk = 550
Na = 152 CO_3 = 240
K = 269 SO_4 = 3340
pH = 9.6
RS $CaCO_3$ = 485
RS $CaSO_4 \cdot 2H_2O$ = 2.21
Filter Press
145 lpm (38.3 gpm)
8.3 lpm (2.2 gpm) 67.6 wt% solids
Recycle Tank
Ca = 1200 Cl = 8
Mg = 2 Alk = 570
Na = 146 CO_3 = 300
K = 251 SO_4 = 2960
pH = 10.2
RS $CaCO_3$ = 596
RS $CaSO_4 \cdot 2H_2O$ = 1.92

Figure 4-6. Summary of Pilot Unit Data from Test 2--Plant 9677.

The high relative saturation values, calculated for the recycle tank effluent, indicate that the potential exists for both calcium carbonate and gypsum precipitation. Although scaling was not positively identified during Test 2, scaling in the recycle line would be expected if operation had continued. The results of Test 2 indicate that the 5-minute reaction/hold tank residence time was not adequate to significantly reduce the scaling potential in the recycle stream.

4.4.2.3 Reaction/Hold Tank (10-Minute Residence Time)--

Test 3 was similar to Test 2 except the reaction tank residence time was increased to 10 minutes. The results of Test 3 are summarized in Figure 4-7.

The results of Test 3 are very similar to the results of Test 2. The concentrations of the major species, except chloride and carbonate, increased across the mix tank. Precipitation of both calcium carbonate and gypsum was indicated from the analytical results and expected based on the relative saturation values. Again, no significant changes in the concentrations of calcium or sulfate occurred across the reaction tank. However, the carbonate concentration increased which could indicate the addition of carbonate through leaching or CO_2 transfer.

Based on the compositions of the reaction tank and the recycle tank effluents, a considerable amount of gypsum precipitation occurred either in the filter press or the recycle tank (probably the filter press). The calculated approach to solid-liquid equilibrium for gypsum was 31 percent for Test 3. The high recycle tank effluent relative saturation values indicate that a potential for precipitation of both gypsum and calcium carbonate existed in the recirculating stream.

4.4.2.4 Summary of Test Results--

The results of the three pilot unit tests at Plant 9677 indicate that the additional 5 to 10 minutes of ash/water contact time are not sufficient to significantly reduce the scaling potential of the recirculating water. In fact, based on the pilot unit data, very little if any additional precipitation occurred in the reaction tank at the increased residence time.

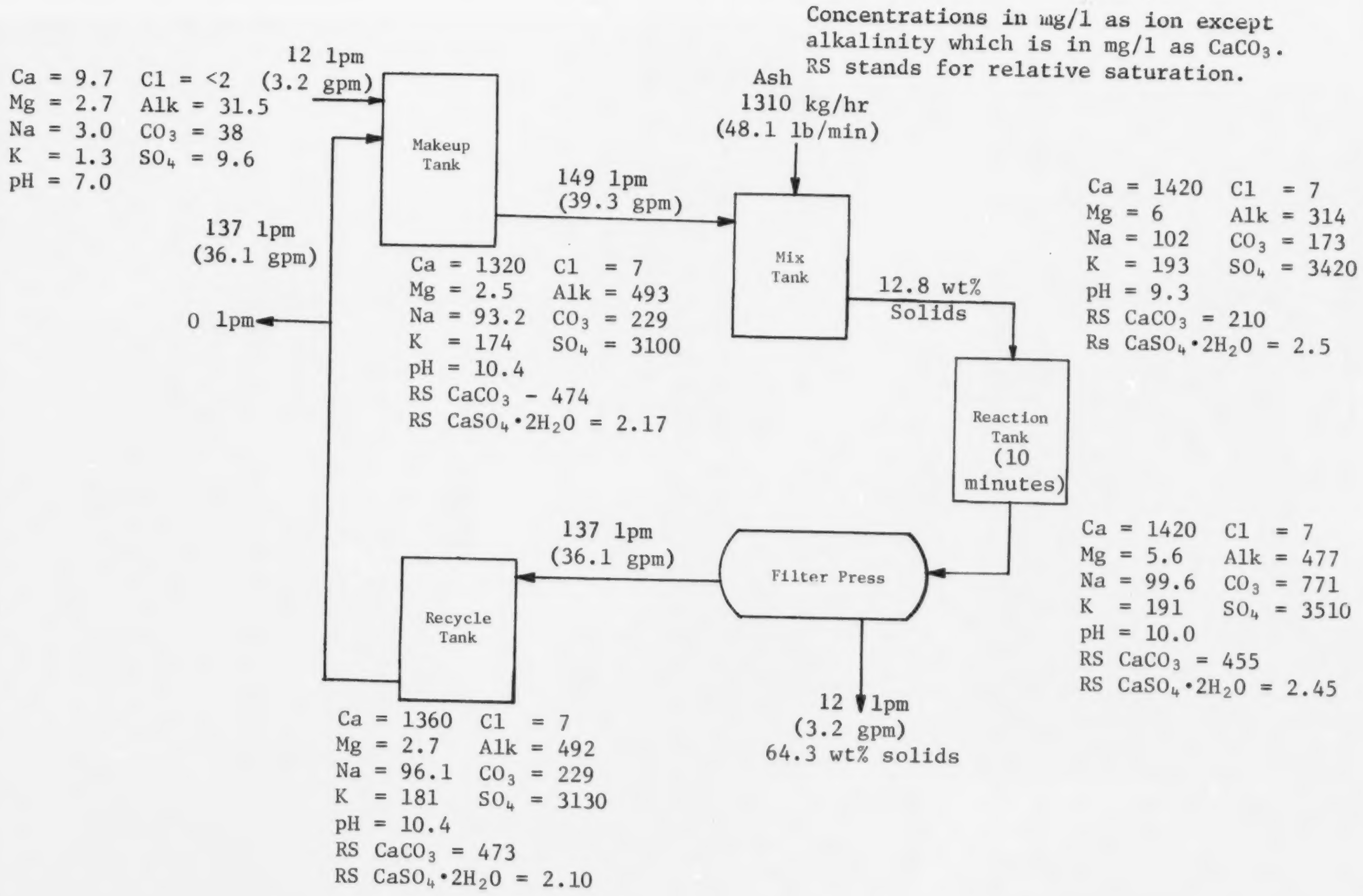

Concentrations in mg/l as ion except alkalinity which is in mg/l as CaCO3. RS stands for relative saturation.
Ca = 9.7 Cl = <2
Mg = 2.7 Alk = 31.5
Na = 3.0 CO3 = 38
K = 1.3 SO4 = 9.6
pH = 7.0
12 lpm (3.2 gpm)
Makeup Tank
137 lpm (36.1 gpm)
0 lpm
149 lpm (39.3 gpm)
Ca = 1320 Cl = 7
Mg = 2.5 Alk = 493
Na = 93.2 CO3 = 229
K = 174 SO4 = 3100
pH = 10.4
RS CaCO3 - 474
RS CaSO4•2H2O = 2.17
Ash
1310 kg/hr
(48.1 lb/min)
Mix Tank
12.8 wt% Solids
Ca = 1420 Cl = 7
Mg = 6 Alk = 314
Na = 102 CO3 = 173
K = 193 SO4 = 3420
pH = 9.3
RS CaCO3 = 210
Rs CaSO4•2H2O = 2.5
Reaction Tank (10 minutes)
Ca = 1420 Cl = 7
Mg = 5.6 Alk = 477
Na = 99.6 CO3 = 771
K = 191 SO4 = 3510
pH = 10.0
RS CaCO3 = 455
RS CaSO4•2H2O = 2.45
Filter Press
137 lpm (36.1 gpm)
12 lpm (3.2 gpm) 64.3 wt% solids
Recycle Tank
Ca = 1360 Cl = 7
Mg = 2.7 Alk = 492
Na = 96.1 CO3 = 229
K = 181 SO4 = 3130
pH = 10.4
RS CaCO3 = 473
RS CaSO4•2H2O = 2.10

Figure 4-7. Summary of Pilot Unit Data from Test 3--Plant 9677.

Precipitation of both calcium carbonate and gypsum occurred in the mix tank. Gypsum also was thought to precipitate in the filter press. Although scaling of either calcium carbonate or gypsum was not positively identified, it would be expected in the recycle line based on the high relative saturation values if operation had continued for longer periods of time. It would not be expected that a full-scale system sluicing a similar ash could be operated in a closed-loop mode based on the pilot unit data. The approach to solid-liquid equilibrium calculated for gypsum for the three pilot unit tests ranged from 31 to 44 percent and averaged 36 percent.

The addition of carbonate from a source other than the makeup water was indicated in all three pilot unit tests. The additional carbonate could be introduced through leaching of carbonate from the ash or from the transfer of CO_2. Based on the high temperatures in the boiler, it would not be expected that significant quantities of carbonate species would be present in the fly ash. For this reason, CO_2 transfer was thought to be the main source of the carbonate. In each of the pilot unit tests, a driving force exists for the absorption of CO_2 in the process water. This is based on the partial pressure of CO_2 in the atmosphere (3.3×10^{-4} atmospheres or 33 Pa). This transfer of CO_2 could be responsible for the calculated pilot unit calcium leachability being somewhat lower than the leachabilities calculated for the pilot and full-scale systems. The quantity of CO_2 transfer occurring (and hence the quantity of calcium precipitating as $CaCO_3$) could not be calculated from the available data.

Based on the low calculated CO_2 partial pressures in the pond water, a driving force for the absorption of CO_2 also existed in the full-scale system. Because of the interactions of the various water systems in the full-scale system, neither the quantity of CO_2 transferring or the quantity of calcium precipitated as $CaCO_3$ in the pond could be calculated. However, the transfer of CO_2 in the full-scale system was not adequate for the pond water to reach CO_2 gas-liquid equilibrium with the atmosphere.

4.4.3 Comparison of Pilot Units Results and Process Model Simulation

Two cases were simulated with the ash sluice system computer model, Tests 1 and 2. The results of the simulations were compared to the pilot unit results to evaluate the ability of the model to accurately predict the operation of the pilot unit.

4.4.3.1 Computer Simulation of Test 1--

As discussed in the previous subsection, based on the measured carbonate values in the pilot unit streams, carbonate was entering the system either through ash leaching or CO_2 transfer. The source and exact quantity of carbonate added to the system could not be identified with the available data. For this reason, Test 1 was simulated in two ways. First, it was assumed that no transfer of CO_2 occurred in the system, and second, the partial pressure of CO_2 in the pilot unit in the recirculating water was input as the partial pressure of CO_2 in equilibrium with the simulation pond. The results of both of these cases are compared with the pilot unit results in Table 4-7.

As shown in Table 4-7, the recirculating water compositions predicted by the model both with and without CO_2 transfer are very similar to the measured composition. The primary differences in both cases are the carbonate and sulfate concentrations.

For the simulation case where CO_2 transfer was not allowed, the predicted carbonate concentration was lower than measured. This indicates that some CO_2 transfer had occurred. The low predicted sulfate value may also result from the fact that the predicted carbonate concentration was less than actually measured. The calculated approach to equilibrium used by the model is the same for both calcium carbonate and gypsum. If carbonate is not available and the relative saturation of gypsum is greater than 1.0, gypsum is assumed to have precipitated. In this circumstance, the model calculated that part of the calcium was precipitated as gypsum when it was actually precipitated as calcium carbonate. Although this will not affect the calculated calcium concentration, it will affect the ratio of calcium carbonate to gypsum precipitated by the model and the predicted concentrations of sulfate and carbonate.

TABLE 4-7. COMPARISON OF COMPUTER MODEL PREDICTIONS TO PILOT UNIT RESULTS - TEST 1.

	Recirculating Water Composition (mg/l)		
		Computer Predicted	
Species	Measured	Without CO_2 Transfer	With CO_2 Transfer
Calcium	1370	1363	1375
Magnesium	11	6.5	10.0
Sodium	86	82	82
Potassium	186	173	173
Chloride	<5	2	2
Carbonate	85[a]	27	220
Sulfate	3450	3050	3250
pH	10.5	11.8	10.8
Relative Saturation			
$CaCO_3$	181[b]	61.4	470
Gypsum	2.5[b]	2.2	2.3

[a] Calculated from measured P- and M- alkalinity values.

[b] Calculated based on measured composition.

Both the pH and the relative saturation values reflect the differences in the measured and predicted sulfate and carbonate concentrations. The lower predicted carbonate value results in a lower calculated calcium carbonate relative saturation value. The lower sulfate value results in the higher predicted pH and lower gypsum relative saturation.

To more accurately simulate the pilot unit operation, a second simulation was performed. In this case, the partial pressure of CO_2 in the pilot unit recirculating water was input as the partial pressure of CO_2 in the pond. The model allows the transfer of CO_2 until the input partial pressure is achieved. This resulted in more accurate sulfate, pH, and gypsum relative saturation values. However, the carbonate value predicted was considerably higher than the measured value. This is because the calculated pH is higher than measured which allows more CO_2 to be absorbed in the model predictions than was actually observed.

The results of the Test 1 simulation cases indicate that the model can adequately simulate the pilot unit in a no treatment configuration. The transfer of CO_2 causes some difficulties during modeling, but the problem appears to be caused by the difficulty in determining the actual quantity of CO_2 transfer in the pilot unit and the accuracy of the calculated carbonate concentrations.

4.4.3.2 Computer Simulation of Test 2--

During Tests 2 and 3, the effect of a reaction/hold tank on the potential for scaling in the recirculating water was investigated. The results of these tests were similar; therefore only the Test 2 results are presented. This case was also simulated with the ash sluice system computer model. The results of this simulation are compared to the pilot unit results in Table 4-8.

As shown in Table 4-8, the predicted concentrations of calcium, sulfate, and carbonate are considerably less than the measured values. This results from the model's prediction that for a 5-minute reaction tank residence time almost 100 percent of the supersaturated species precipitate. As discussed in the previous subsection, this was not the case. In fact, based on the pilot unit data very little, if any, precipitation occurred in the reaction tank. This inconsistency requires a re-examination of the precipitation rate constants used in the model.

TABLE 4-8. COMPARISON OF COMPUTER MODEL PREDICTIONS WITH PILOT UNIT RESULTS AT PLANT 9677 - TEST 2.

	Recirculating Water Composition (mg/l)	
Species	Measured	Computer Predicted
Calcium	1200	753
Magnesium	2	<1
Sodium	146	147
Potassium	251	253
Chloride	8	8
Carbonate	300	0.6
Sulfate	2960	1658
pH	10.2	11.9
Relative Saturation		
$CaCO_3$	596[a]	1.01
Gypsum	1.92[a]	1.00

[a] Calculated based on measured composition.

4.5 PILOT UNIT TESTING AT PLANT 9991

Pilot unit testing was conducted at Plant 9991 during the fall of 1982. Fly ash collected at the plant during this time period was used for pilot unit testing. Makeup water to the plant's full-scale bottom and fly ash sluice system, which consisted of treated wastewater (primarily demineralizer regeneration waste), was used as makeup water to the pilot unit. The following test conditions were examined at Plant 9991 with pH adjustment at reduced blowdown rates:

Test	Slurry Weight Percent Solids	Treatment Technique
1	5	100 percent blowdown
2	10	100 percent blowdown
3	5	pH adjustment (H_2SO_4)
4	5	pH adjustment (HCl)
5	10	pH adjustment (HCl)
6	10	pH adjustment (H_2SO_4)

The discussion in this section presents the results of pilot unit testing at Plant 9991. First, fly ash leaching test data are presented. Then, the results of the pilot unit test program are discussed. Operating conditions predicted by the ash sluice computer model are compared with pilot unit results to evaluate the ability of the model to simulate operating systems. Finally, pilot unit test results are compared to the full-scale system operation to evaluate the feasibility of achieving closed-loop operation without encountering scale formation.

4.5.1 Fly Ash Leaching

The leachability of soluble species from the fly ash during ash transport is one of the most important variables affecting test results. However, it is one of the most difficult variables to accurately determine under all of the conditions that are encountered during pilot unit testing. Therefore, several data sets were examined to determine the variability of the ash leach data and to identify the most appropriate data for evaluation purposes.

The data sets used to estimate ash leachability include laboratory leaching results, pilot unit test results, and full-scale system characterization data at Plant 9991. Samples were collected during two different time periods: 1) during a preliminary site visit and 2) during pilot unit testing. These results are discussed below.

4.5.1.1 Data From Preliminary Site Visit--

During a preliminary site visit to Plant 9991 in August 1982 prior to pilot unit testing, samples of the fly ash and plant ash transport process streams were collected. The samples were sent to the laboratory for analysis and fly ash leaching tests were conducted. The leaching tests investigated two different ash slurry concentrations in deionized water. Leaching was conducted over approximately a 2-hour period and the pH was monitored. Initially, the pH changed indicating that species were being leached from the ash. When the pH became stable, the composition of the slurry water was determined and the amount of species leached from the ash was correlated to the amount of ash present in the slurry. Leaching test procedures were discussed in more detail in Section 4.4.

Material balances were calculated for major species in the full-scale fly ash sluice system to estimate the amount of soluble species that were leached from the fly ash during sluicing operations. The estimates of leachable species in the full-scale system are compared to laboratory fly ash leaching results in Table 4-9. The estimated leachability of calcium compares very well with laboratory data. Leachabilities of some of the other species, such as sodium and sulfate, were higher by about a factor of two in the full-scale system versus the laboratory results. Considering the variability of operation in the full-scale system (e.g., changing makeup water sources and compositions, changing ash compositions and transport rate), the values compare reasonably well.

The relative saturations of calcium carbonate and magnesium hydroxide are greater than 1.0, indicating that the potential for precipitation of these species exists. The very low calculated leachability of magnesium in the

TABLE 4-9. COMPARISON OF LABORATORY FLY ASH LEACH TEST RESULTS WITH APPARENT FULL-SCALE LEACHING DURING PRELIMINARY SITE VISIT TO PLANT 9991 IN AUGUST 1982

	Laboratory Results mg/g ash		Full-Scale Results mg/g ash
Ash Slurry	9.1 wt%	6.5 wt%	3.6 wt%
Species			
Calcium	8.1	8.7	8.6
Magnesium	0.003	0.001	0.15
Sodium	0.40	0.37	0.88
Potassium	0.05	0.04	0.05
Chloride	0.05	0.02	0.35
Sulfate	3.6	3.6	6.6
Carbonate	0.05	0.07	–[a]
Final pH	12.3	12.4	11.3
Relative Saturation			
Calcium Carbonate	8.1	7.74	26.6
Gypsum	0.30	0.18	0.3
Magnesium Hydroxide	21.3	14.5	74.0

[a] Negligible

laboratory tests is probably due to the fact that some magnesium reprecipitated as magnesium hydroxide. Some calcium carbonate may have precipitated, but the amount of carbonate present in the system was probably too low to have affected the relatively high calcium leachability estimates significantly.

Another factor that can affect the amount of species leached using laboratory procedures compared to actual leaching encountered during pilot and full-scale operation is the leaching rate of the various species. Laboratory leaching rate data are presented in Figure 4-8. These results indicate that all of the sodium leached from the ash occurs in less than one minute. Likewise, sulfate leaches from the ash quite rapidly. However, calcium is leached at a slower rate. Considerably more calcium has been leached after three minutes than after one minute. The data may also indicate that calcium is decreasing or precipitating at longer time periods although the apparent decrease is small. Sulfate levels also appear to decrease at longer time periods, but the apparent decrease is even less than calcium. If calcium is precipitating, then the leachable fraction of calcium determined by this laboratory procedure will underestimate the actual amount of calcium leached.

4.5.1.2 Data Collected During Pilot Unit Testing--

Ash leaching data were also collected during pilot unit testing from three sources: 1) field laboratory leaching tests, 2) pilot unit results, and 3) full-scale system characterization at Plant 9991. Data from all three sources are based on samples collected during pilot unit testing so that the composition of fly ash and makeup water from each source should be similar. However, some differences could exist as compositions of ash and makeup water fluctuated during the test period.

Fly ash samples were leached in the field laboratory at two different ash slurry concentrations. Deionized water was used to prepare a 5 weight percent ash slurry and pilot unit makeup water was used to prepare a 10 weight percent ash slurry. Otherwise the field laboratory leaching procedures were the same as those described earlier for testing conducted at Radian's Austin laboratory. Samples of the process streams collected during pilot unit testing were

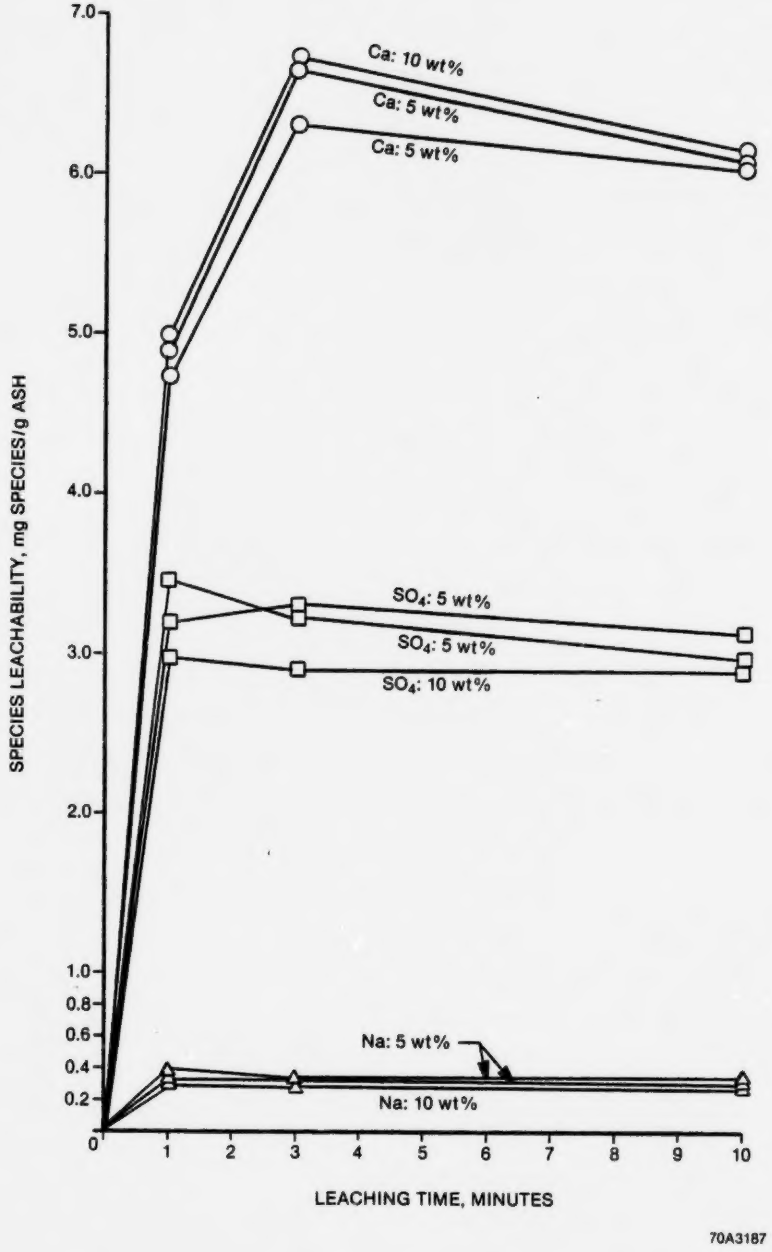


Figure 4-8. Laboratory Leaching Rate Data for Plant 9991.

analyzed, and the results were used to estimate ash leaching by performing material balance calculations for the six tests. Samples of the full-scale ash handling system at Plant 9991 were also collected on six separate occasions during the period when pilot unit testing was conducted.

Ash leaching data from the three sources are summarized in Table 4-10. Both the average and range of estimates are presented. In general, averages of the estimated values for all of the species from each source compare reasonably well. The most important discrepancy is the estimated quantity of calcium leached from each of the sources since the quantity is large compared to the other species and slightly soluble calcium salts can form scale. Ranges in estimates can result from 1) variations in ash composition between tests and 2) errors in measurements of sluice water composition and flow rate. An error propagation analysis indicates that a variability of ±20 percent can be expected due to measurement errors. The variability in ash composition between tests was not determined.

The quantity of calcium leached during the field laboratory tests is very similar to results presented earlier in Table 4-9 based on samples collected during the preliminary visit. However, estimates of the quantity of calcium leached based on pilot-unit and full-scale characterization data are substantially less than the field laboratory results.

Relative saturations for calcium carbonate and gypsum indicate that calcium carbonate was supersaturated and gypsum was subsaturated (except for pilot unit Test 3). The estimate of calcium leachability could have been affected if leached calcium was precipitated as calcium carbonate during the tests. Since the laboratory apparatus was covered to minimize absorption of CO_2 from the atmosphere, the levels of carbonate were so low that the quantity of calcium carbonate that could have been precipitated would have been minimal. More opportunity for CO_2 transfer and subsequent calcium carbonate precipitation existed in the pilot plant, and the greatest opportunity for transfer was in the ash ponds of the full-scale system.

TABLE 4-10. SUMMARY OF ASH LEACHING DATA--PLANT 9991.

	Quantity Leached, mg/g ash							Relative Saturation	
Data Source	Calcium	Magnesium	Sodium	Potassium	Chloride	Sulfate	Slurry pH	Calcium Carbonate	Gypsum
Field Laboratory									
- average	8.1	-	0.37	0.03	0.03	3.7		7.9	0.2
- range	6.2-9.9	-	0.23-0.51	0.0-0.06	0.0-0.06	3.2-4.2	12.2-12.7	7.7-8.1	0.1-0.3
Full-Scale System									
- average	4.0	-	0.43	0.02	0.08	3.0		94	0.3
- range	1.8-7.8	-	0.23-0.78	0.01-0.02	0.08[a]	1.1-7.0	11.1-12.4	65-120	0.2-0.4
Pilot Unit									
- average	5.7	-	0.40	0.05	0.12	2.5		110	0.6
- range	3.5-8.1	-	0.24-0.73	0.04-0.08	0.12[b]	1.9-3.0	11.8-12.6	50-150	0.2-1.3[c]

[a] Based on results from data collected on October 22, 1982.

[b] Based on Test 6 results only.

[c] Gypsum was subsaturated in every test except Test 3.

The greatest uncertainty in ash leaching data is for the estimates prepared from full-scale data. Because the full-scale ash handling system transports both fly ash and bottom ash, material balance calculations were based on the change in sluice water composition during fly ash transport. The residence time of the fly ash in the transport line is only a few minutes, but calcium leaches at a slower rate than the other species as indicated earlier in Figure 4-8. Therefore, the calcium values based on the full-scale system may be lower due to the reduced contact time of ash and water. Also, the ash content in the fly ash slurry discharge was not measured. As a result, leachability estimates are based on design slurry characteristics (5 weight percent). Fluctuations in the ash content of the slurry could be responsible for fluctuations in the leaching estimates.

In summary, leachability data from all of the data sources compare reasonably well. The greatest uncertainties in the accuracies of estimates are for the pilot- and full-scale systems. Furthermore, use of the higher estimates for calcium and sulfate from the laboratory leaching data as input to the ash sluice model will result in a somewhat more conservative estimate of potential scaling conditions. Therefore, laboratory data are sufficiently conservative to provide a safety factor in designing ash handling systems that will enable reliable operation to be achieved.

4.5.2 Results of Pilot Tests

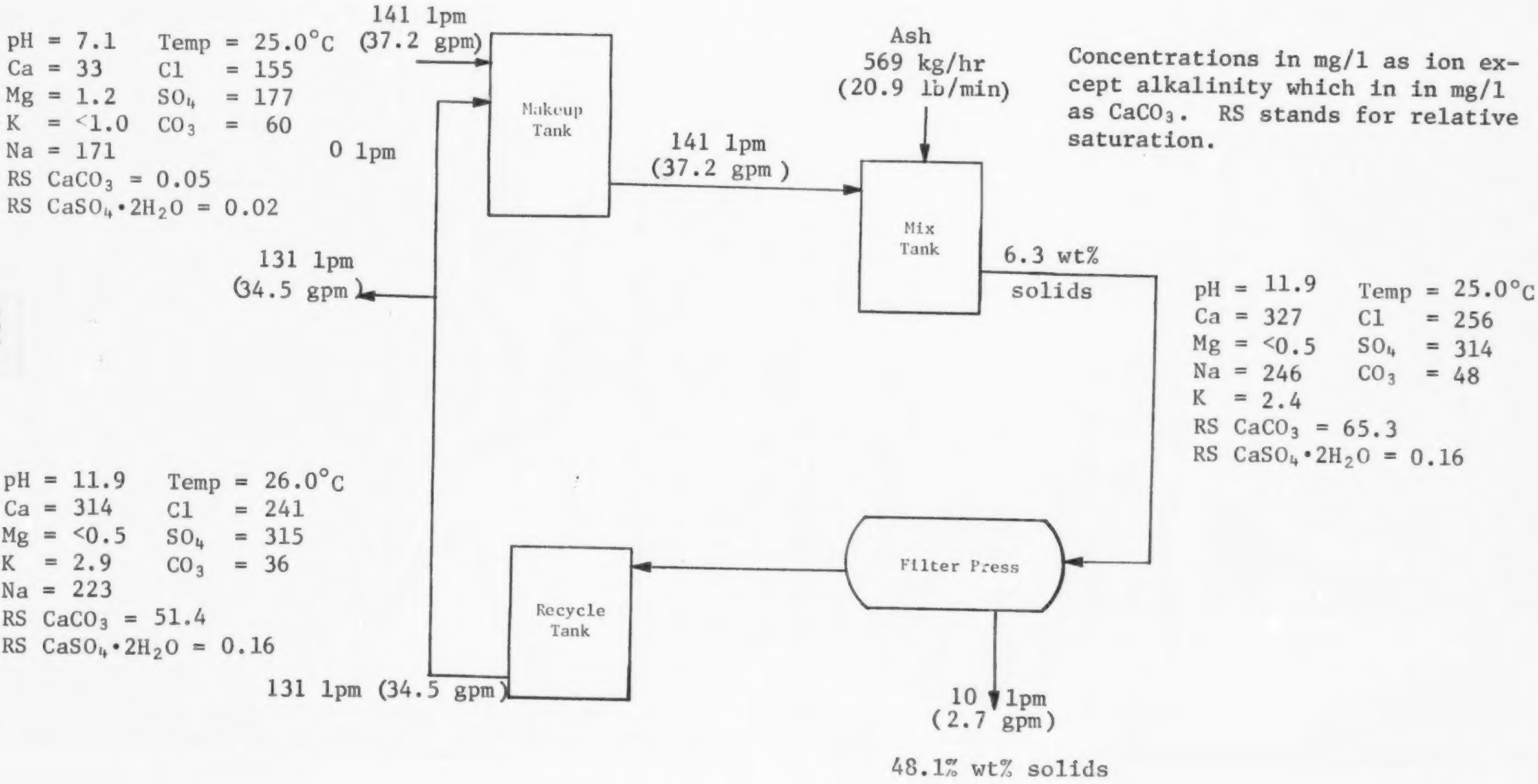
Baseline tests were conducted first with no water treatment to control scale formation. None of the ash transport water was recycled during baseline testing because the potential for calcium carbonate scale formation was encountered. Then, tests using sulfuric and hydrochloric acid to adjust the pH of recirculating water to control calcium carbonate scale formation were conducted. Ash transport water was recycled to slurry fly ash during these tests. The results of the tests are discussed below.

4.5.2.1 Baseline Pilot Tests - No Treatment--

Tests were conducted with no treatment and no recirculation of transport water at approximately 5- and 10-weight percent fly ash in the slurry. All of the transport water that was separated from the ash by the filter press was discharged from the system as blowdown. Conductivity and pH of the system blowdown were monitored to determine the stability of pilot plant operation. When stable operation was achieved, samples from all of the process streams were collected, filtered, and preserved to prevent further reactions from taking place before the samples could be analyzed. The samples were analyzed to determine the liquid phase composition of the process streams. The compositions were input to the chemical equilibrium model to estimate the relative saturations of potentially precipitating species.

The results of Test 1, baseline conditions at 6.3-weight percent ash, are summarized in Figure 4-9. All of the species present in the makeup water increased in concentration after contact with fly ash in the mix tank except magnesium and carbonate, which decreased. At the high pH of the slurry, magnesium probably precipitated as magnesium hydroxide and carbonate precipitated as calcium carbonate. Some calcium may have precipitated after the slurry exited the mix tank and prior to discharge, but the small apparent decrease in calcium concentration is within analytical error. While gypsum relative saturation was less than 1.0, the relative saturation of calcium carbonate was greater than 50, indicating that the potential for calcium carbonate precipitation exists in the blowdown line.

The results of Test 2, baseline conditions at 8.8 weight percent ash, are summarized in Figure 4-10. In Test 2, all of the species present in the makeup water increased in the slurry water except for magnesium and carbonate. Once again, magnesium probably precipitated as magnesium hydroxide and carbonate precipitated as calcium carbonate. The calcium concentration was higher in the blowdown than the mix tank effluent, indicating that additional leaching occurred in the filter press at a faster rate than calcium carbonate precipitated. Gypsum relative saturations in the system were less than 1.0, indicating that the potential gypsum precipitation did not exist. Calcium carbonate relative saturation in the blowdown was calculated to be 102, which was nearly twice as high as the Test 1 results.


141 lpm
(37.2 gpm)
pH = 7.1 Temp = 25.0°C
Ca = 33 Cl = 155
Mg = 1.2 SO₄ = 177
K = <1.0 CO₃ = 60
Na = 171
RS CaCO₃ = 0.05
RS CaSO₄•2H₂O = 0.02
0 1pm
Makeup Tank
141 lpm
(37.2 gpm)
Ash
569 kg/hr
(20.9 lb/min)
Mix Tank
6.3 wt%
solids
pH = 11.9 Temp = 25.0°C
Ca = 327 Cl = 256
Mg = <0.5 SO₄ = 314
Na = 246 CO₃ = 48
K = 2.4
RS CaCO₃ = 65.3
RS CaSO₄•2H₂O = 0.16
131 lpm
(34.5 gpm)
pH = 11.9 Temp = 26.0°C
Ca = 314 Cl = 241
Mg = <0.5 SO₄ = 315
K = 2.9 CO₃ = 36
Na = 223
RS CaCO₃ = 51.4
RS CaSO₄•2H₂O = 0.16
Recycle Tank
Filter Press
131 lpm (34.5 gpm)
10 lpm
(2.7 gpm)
48.1% wt% solids

Concentrations in mg/l as ion except alkalinity which in in mg/l as $CaCO_3$. RS stands for relative saturation.

Figure 4-9. Summary of Pilot Unit Data from Test 1--Plant 9991.

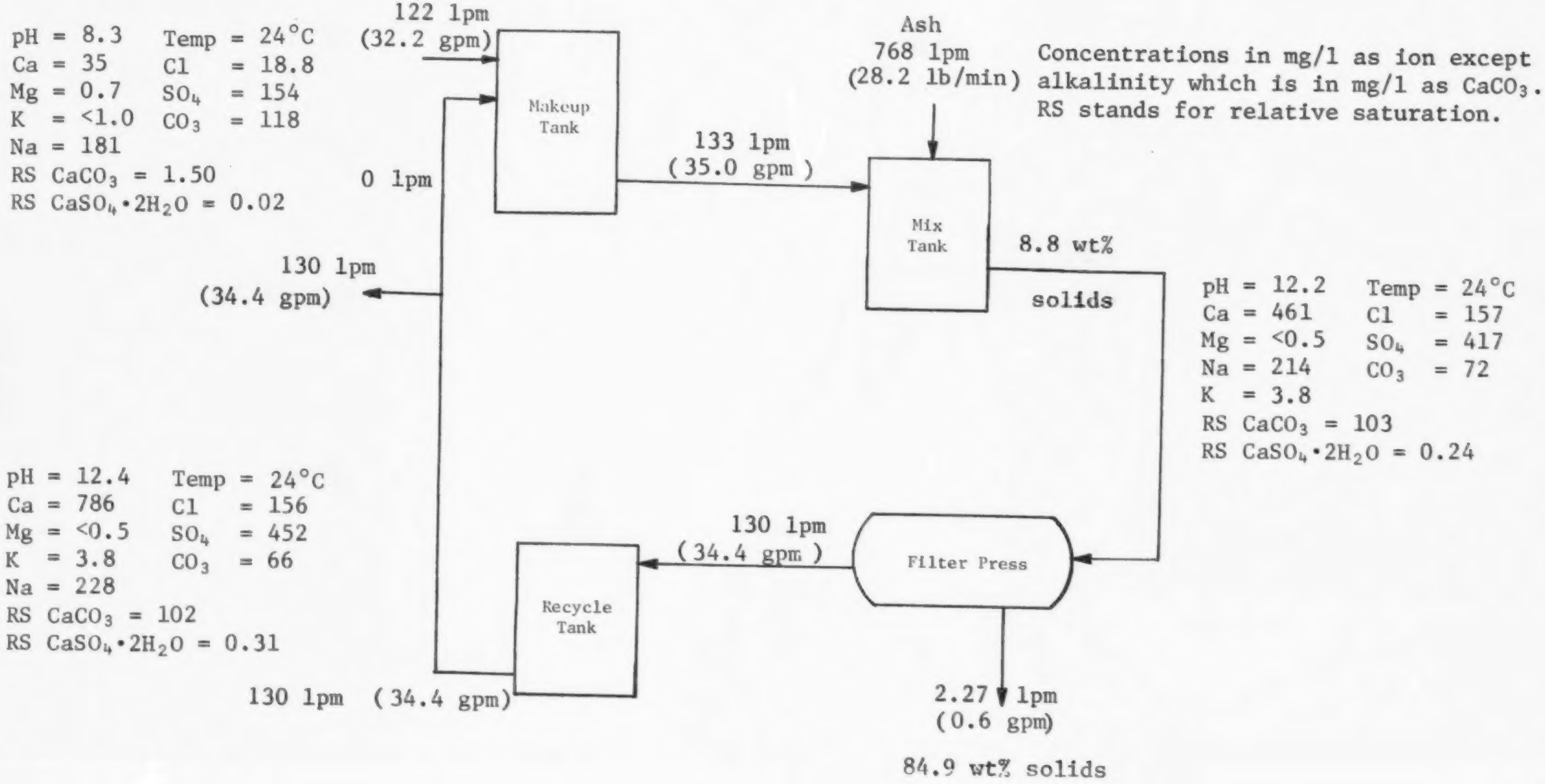

pH = 8.3 Temp = 24°C
Ca = 35 Cl = 18.8
Mg = 0.7 SO4 = 154
K = <1.0 CO3 = 118
Na = 181
RS CaCO3 = 1.50
RS CaSO4•2H2O = 0.02
122 lpm
(32.2 gpm)
Makeup Tank
0 lpm
130 lpm
(34.4 gpm)
133 lpm
(35.0 gpm)
Ash
768 lpm
(28.2 lb/min)
Mix Tank
Concentrations in mg/l as ion except alkalinity which is in mg/l as CaCO3.
RS stands for relative saturation.
8.8 wt%
solids
pH = 12.2 Temp = 24°C
Ca = 461 Cl = 157
Mg = <0.5 SO4 = 417
Na = 214 CO3 = 72
K = 3.8
RS CaCO3 = 103
RS CaSO4•2H2O = 0.24
Filter Press
130 lpm
(34.4 gpm)
Recycle Tank
pH = 12.4 Temp = 24°C
Ca = 786 Cl = 156
Mg = <0.5 SO4 = 452
K = 3.8 CO3 = 66
Na = 228
RS CaCO3 = 102
RS CaSO4•2H2O = 0.31
130 lpm (34.4 gpm)
2.27 lpm
(0.6 gpm)
84.9 wt% solids

Figure 4-10. Summary of Pilot Unit Data from Test 2--Plant 9991.

In summary, baseline results from Tests 1 and 2 indicate that the fly ash can be transported in excess of 10-weight percent ash without encountering gypsum scale formation when none of the transport water is recycled in the system. However, the potential for calcium carbonate and magnesium hydroxide scale formation existed due to the alkaline ash and high pH in the system. A large amount of calcium was leached from the ash, but only a small amount of carbonate was introduced into the pilot plant by the makeup water. Furthermore, only a relatively small portion of the carbonate precipitated as calcium carbonate. In a full-scale system where ponds are used for dewatering, the amount of carbonate introduced to the system from other sources (e.g., atmospheric CO_2 transfer) could be greater, so that the amount of calcium carbonate precipitated could be increased. In Test 1, approximately 40 percent of the supersaturated calcium carbonate appeared to precipitate based on overall material balance calculations, while in Test 2 approximately 43 percent was estimated to have precipitated. Since all of the supersaturated calcium carbonate did not precipitate in the mix tank, slurry line or dewatering equipment, acid addition to control calcium carbonate scale formation in the recycle line was investigated.

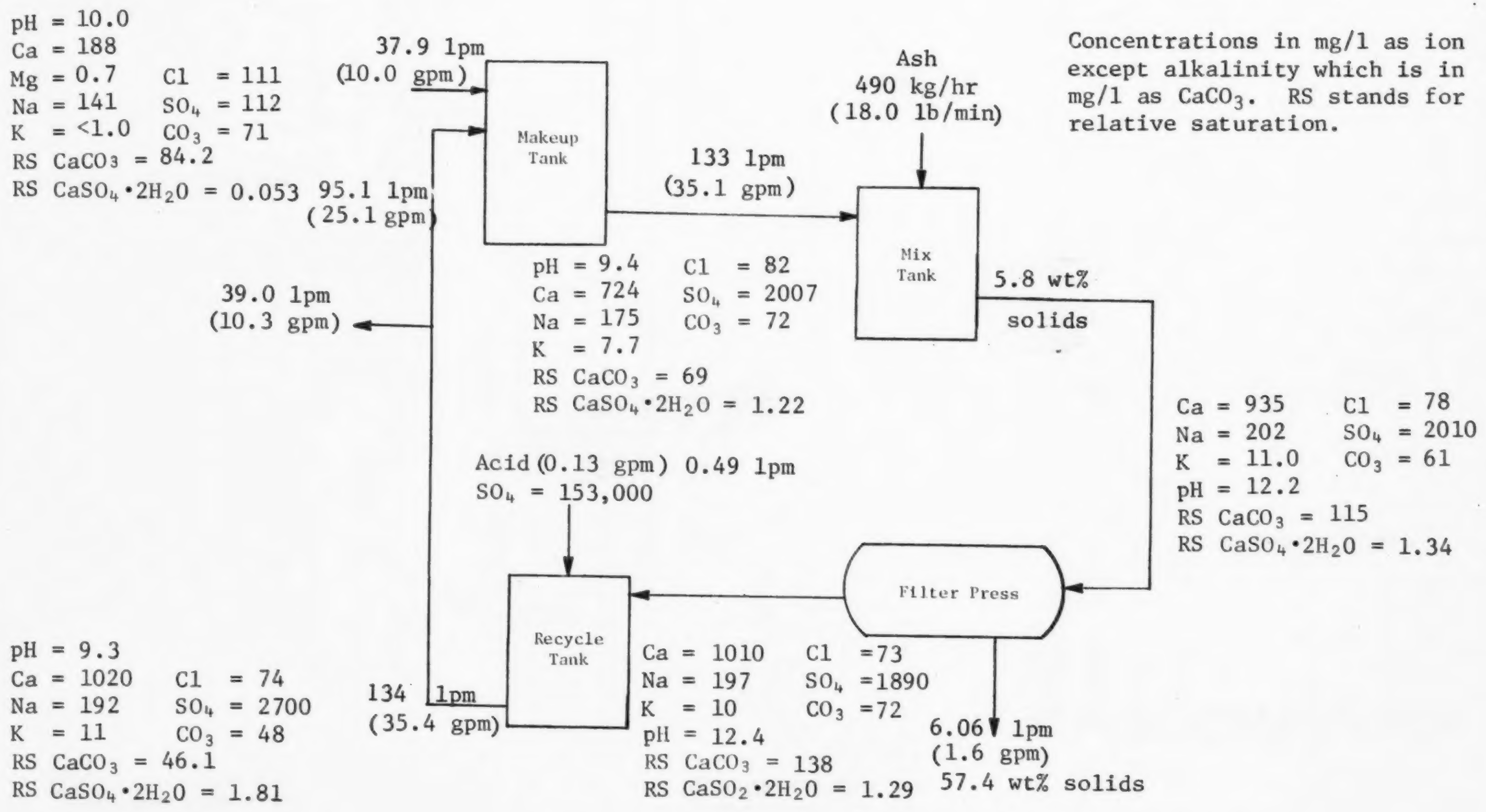
4.5.2.2 Acid Adjustment at 5 Weight Percent Ash--

To evaluate a means of controlling calcium carbonate scale formation, sulfuric and hydrochloric acid were used to adjust the pH of the transport water. After ash was filtered from the slurry in Tests 3 and 4, a portion of the pH adjusted transport water was recycled to the makeup tank and reused to slurry fly ash at approximately 5 weight percent. The tendency of gypsum to precipitate in the system was increased by recycling transport water. Use of sulfuric acid further increased the gypsum relative saturation by increasing sulfate levels in the return water. Hydrochloric acid was investigated as an alternative to control calcium carbonate scale formation without contributing to increased sulfate levels.

In Test 3, a 5.8 weight percent fly ash slurry was tested and sulfuric acid was used to adjust the pH of the transport water after ash was removed from the slurry by the filter press. About 70 percent of the transport water was recycled to the makeup tank and reused to slurry fly ash. The results of Test 3 are summarized in Figure 4-11.

At 70 percent recycle, the gypsum relative saturation of the makeup water sent to the mix tank was approximately 1.22. After contact with fly ash, the gypsum relative saturation in the slurry water discharged from the mix tank increased to 1.34. However, the gypsum relative saturation of the transport water after filtration decreased to about 1.29, indicating that gypsum had precipitated in the system. These results are very consistent with previous studies of gypsum precipitation (refer to Appendix E) which indicate that precipitation by secondary nucleation occurs at relative saturations between 1.3 and 1.4. Correspondingly, sulfate levels were observed to decrease by about 6 percent between exiting the mix tank and the filter press, but the calcium level increased by 8 percent. These results indicate that gypsum was precipitating in the system and that calcium was continuing to be leached from the ash in the filter press. Since some gypsum may also have precipitated in the mix tank, it is not possible to accurately determine the total amount of gypsum that precipitated in Test 3. If an average sulfate leachability is assumed from the other tests, material balance calculations indicate that a quantity of sulfate equivalent to all of the sulfate leached from the ash and a portion of sulfate added as sulfuric acid for pH adjustment precipitated in the system.

The difference in measured carbonate values from the makeup tank compared to the blowdown indicate that approximately 40 percent of the supersaturated calcium carbonate also precipitated in the system. The relative saturation of calcium carbonate after pH adjustment remained well above 1.0, indicating that a lower pH would be required to completely eliminate the potential for calcium carbonate scale formation in the recycle line. Based on computer calculations, a pH between 7.0 and 7.5 would be adequate to reduce the relative saturation of calcium carbonate to 1.0 or less.



pH = 10.0
Ca = 188
Mg = 0.7
Na = 141
K = <1.0
Cl = 111
SO_4 = 112
CO_3 = 71
RS $CaCO_3$ = 84.2
RS $CaSO_4 \cdot 2H_2O$ = 0.053
37.9 lpm
(10.0 gpm)
95.1 lpm
(25.1 gpm)
Makeup Tank
39.0 lpm
(10.3 gpm)
133 lpm
(35.1 gpm)
pH = 9.4
Ca = 724
Na = 175
K = 7.7
Cl = 82
SO_4 = 2007
CO_3 = 72
RS $CaCO_3$ = 69
RS $CaSO_4 \cdot 2H_2O$ = 1.22
Ash
490 kg/hr
(18.0 lb/min)
Mix Tank
5.8 wt%
solids
Concentrations in mg/l as ion except alkalinity which is in mg/l as $CaCO_3$. RS stands for relative saturation.
Ca = 935
Na = 202
K = 11.0
Cl = 78
SO_4 = 2010
CO_3 = 61
pH = 12.2
RS $CaCO_3$ = 115
RS $CaSO_4 \cdot 2H_2O$ = 1.34
Acid (0.13 gpm) 0.49 lpm
SO_4 = 153,000
Filter Press
Recycle Tank
Ca = 1010
Na = 197
K = 10
Cl =73
SO_4 =1890
CO_3 =72
pH = 12.4
RS $CaCO_3$ = 138
RS $CaSO_2 \cdot 2H_2O$ = 1.29
6.06 lpm
(1.6 gpm)
57.4 wt% solids
pH = 9.3
Ca = 1020
Na = 192
K = 11
Cl = 74
SO_4 = 2700
CO_3 = 48
RS $CaCO_3$ = 46.1
RS $CaSO_4 \cdot 2H_2O$ = 1.81
134 lpm
(35.4 gpm)

Figure 4-11. Summary of Pilot Unit Data from Test 3--Plant 9991.

In Test 4 with a 5.9 weight percent ash slurry, hydrochloric acid was used to adjust the pH of the transport water. The results are summarized in Figure 4-12. Approximately 78 percent of the transport was recycled and reused to slurry fly ash. Even at the slightly higher recycle rate, gypsum remained subsaturated at all points in the system due to the reduced sulfate levels when hydrochloric acid was used instead of sulfuric acid as in Test 3.

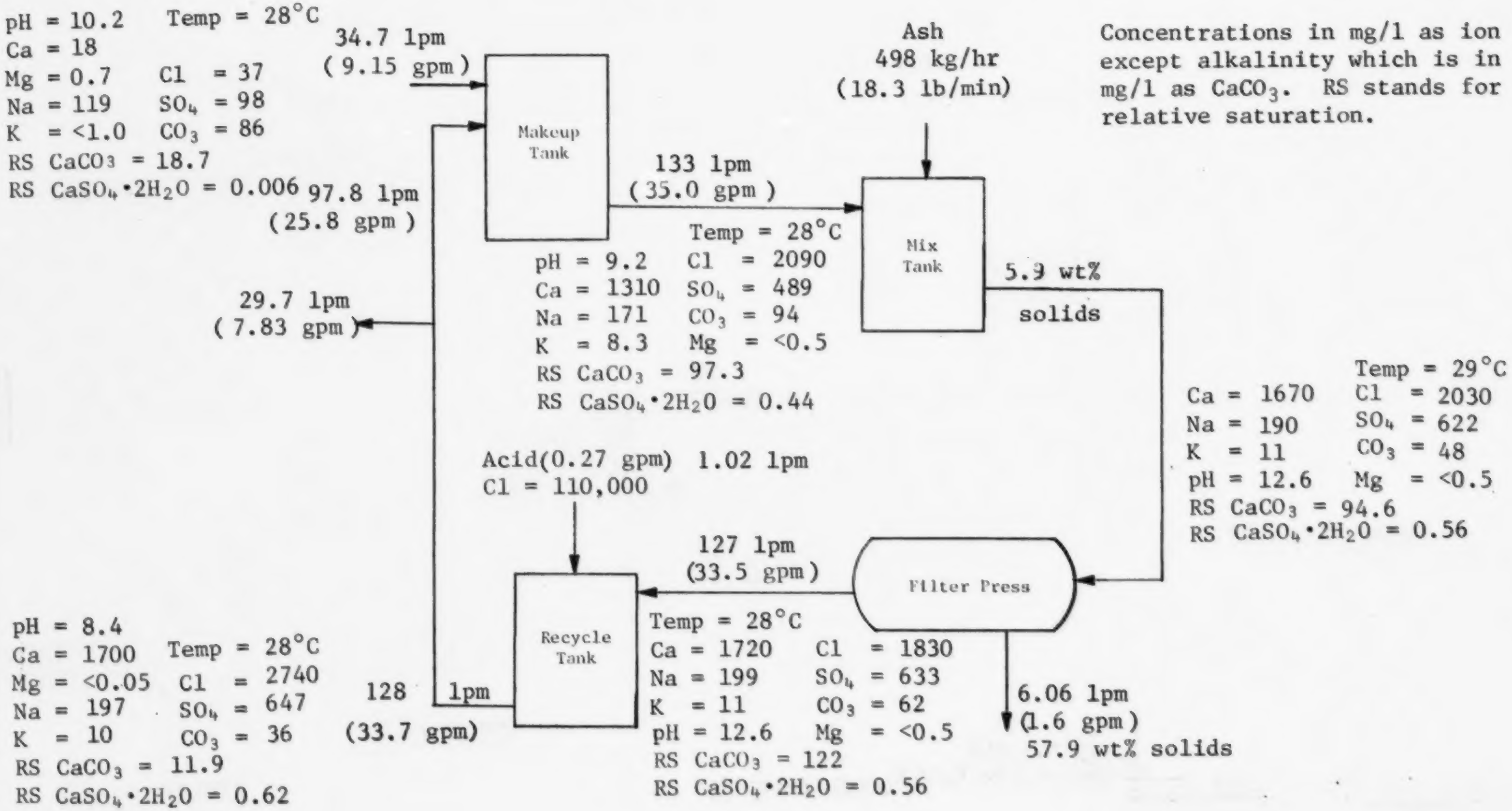
Once again, some carbonate appeared to precipitate in the system based on material balance calculations (approximately 60 percent of the supersaturated calcium carbonate). Likewise, most of the calcium leaching from the ash occurred in the mix tank and some additional leaching may have occurred in the filter press. Again, the pH of the blowdown introduced was not reduced to low enough levels to completely eliminate the potential for calcium carbonate scale formation in the recycle line.

Comparison of results between Tests 3 and 4 indicate that approximately 25 percent of the total calcium entering the ash transport system precipitated in Test 3 (mostly as gypsum) using sulfuric acid, while less than one percent precipitated in Test 4 (mostly calcium carbonate) at similar operating conditions.

In summary, recycling 70 percent of the transport water resulted in substantial precipitation of gypsum when sulfuric acid was used for pH adjustment. However, use of hydrochloric acid essentially eliminated gypsum precipitation at 78 percent recycle and higher recycle rates could have been achieved before gypsum scale was encountered. Nevertheless, pH must be adjusted to lower levels to completely eliminate the potential for calcium carbonate scale formation in the return line.

4.5.2.3 Acid Adjustment at 10 Weight Percent Ash--

In tests similar to Tests 3 and 4, hydrochloric and sulfuric acid were used to adjust the pH of the transport water which was partially recycled to slurry fly ash at approximately 10 weight percent solids.


pH = 10.2 Temp = 28°C
Ca = 18
Mg = 0.7 Cl = 37
Na = 119 SO₄ = 98
K = <1.0 CO₃ = 86
RS CaCO₃ = 18.7
RS CaSO₄·2H₂O = 0.006
34.7 lpm
(9.15 gpm)
Makeup Tank
97.8 lpm
(25.8 gpm)
29.7 lpm
(7.83 gpm)
133 lpm
(35.0 gpm)
Ash
498 kg/hr
(18.3 lb/min)
Mix Tank
Temp = 28°C
pH = 9.2 Cl = 2090
Ca = 1310 SO₄ = 489
Na = 171 CO₃ = 94
K = 8.3 Mg = <0.5
RS CaCO₃ = 97.3
RS CaSO₄·2H₂O = 0.44
5.9 wt% solids
Temp = 29°C
Ca = 1670 Cl = 2030
Na = 190 SO₄ = 622
K = 11 CO₃ = 48
pH = 12.6 Mg = <0.5
RS CaCO₃ = 94.6
RS CaSO₄·2H₂O = 0.56
Acid(0.27 gpm) 1.02 lpm
Cl = 110,000
127 lpm
(33.5 gpm)
Filter Press
Recycle Tank
Temp = 28°C
Ca = 1720 Cl = 1830
Na = 199 SO₄ = 633
K = 11 CO₃ = 62
pH = 12.6 Mg = <0.5
RS CaCO₃ = 122
RS CaSO₄·2H₂O = 0.56
6.06 lpm
(1.6 gpm)
57.9 wt% solids
pH = 8.4
Ca = 1700 Temp = 28°C
Mg = <0.05 Cl = 2740
Na = 197 SO₄ = 647
K = 10 CO₃ = 36
RS CaCO₃ = 11.9
RS CaSO₄·2H₂O = 0.62
128 lpm
(33.7 gpm)

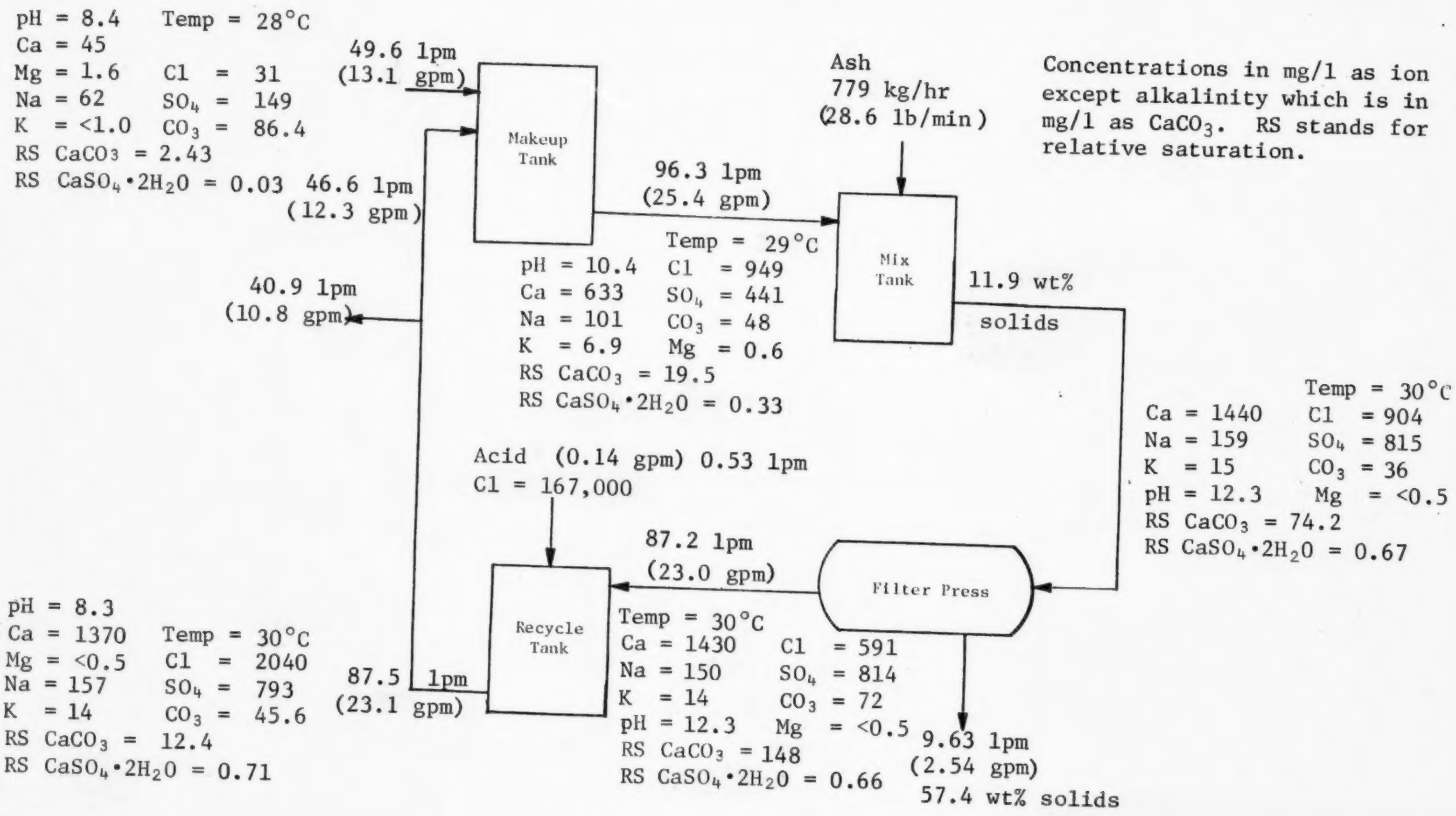
Concentrations in mg/l as ion except alkalinity which is in mg/l as $CaCO_3$. RS stands for relative saturation.

Figure 4-12. Summary of Pilot Unit Data from Test 4--Plant 9991.

The results of Test 5 with hydrochloric acid addition for pH adjustment are summarized in Figure 4-13. Approximately 56 percent of the transport water was recycled to slurry fly ash at 11.9 weight percent ash. Use of hydrochloric acid allowed the gypsum relative saturation to be maintained at about 0.7 at that recycle rate. Because the gypsum relative saturation was less than 1.0, additional ash transport water could have been recycled without gypsum scale formation. In Test 5, approximately 56 percent of the supersaturated calcium carbonate was estimated to have precipitated. Once again, the pH would have to be adjusted to lower levels to completely eliminate the potential for calcium carbonate scale.

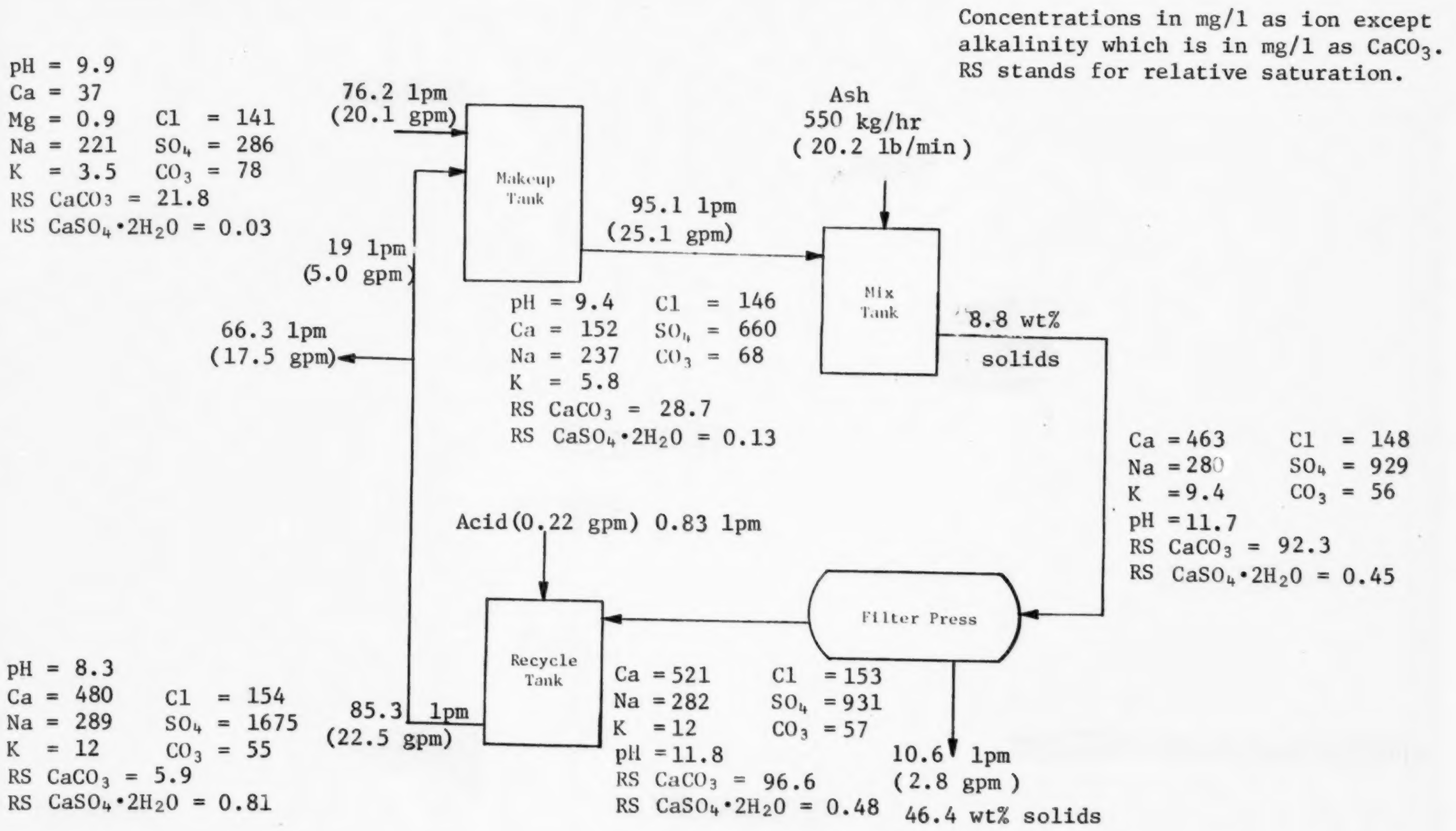
In Test 6 using sulfuric acid for pH adjustment, only 27 percent of the ash transport water was recycled to slurry fly ash at 8.8 weight percent ash. The results are summarized in Figure 4-14. This recycle rate was adequate to maintain gypsum relative saturation in the recycle line at about 0.81. While a slightly higher recycle rate could have been attempted without encountering gypsum scale formation, the operating conditions tested provide a reasonable safety margin for process upsets and variations in makeup and fly ash composition. Once again, some calcium carbonate appears to have precipitated in the mix tank where most of the calcium is leached from the ash. A small amount of calcium appears to have been leached in the filter press and a minor amount of calcium carbonate may have also precipitated there (approximately 35 percent overall). Also, calcium carbonate remained slightly supersaturated after pH adjustment to 8.3.

In summary, less transport water could be recycled while preventing gypsum scale formation when slurries containing higher levels of ash were used. Once again, pH must be adjusted to lower levels to completely eliminate potential for calcium carbonate scale formation in the recycle line. Use of hydrochloric acid instead of sulfuric acid allowed more transport water to be recycled before encountering gypsum scale formation.


pH = 8.4 Temp = 28°C
Ca = 45
Mg = 1.6 Cl = 31
Na = 62 SO_4 = 149
K = <1.0 CO_3 = 86.4
RS $CaCO_3$ = 2.43
RS $CaSO_4 \cdot 2H_2O$ = 0.03
49.6 lpm
(13.1 gpm)
46.6 lpm
(12.3 gpm)
Makeup Tank
40.9 lpm
(10.8 gpm)
96.3 lpm
(25.4 gpm)
pH = 10.4
Ca = 633
Na = 101
K = 6.9
Temp = 29°C
Cl = 949
SO_4 = 441
CO_3 = 48
Mg = 0.6
RS $CaCO_3$ = 19.5
RS $CaSO_4 \cdot 2H_2O$ = 0.33
Ash
779 kg/hr
(28.6 lb/min)
Mix Tank
11.9 wt%
solids
Temp = 30°C
Ca = 1440
Na = 159
K = 15
pH = 12.3
Cl = 904
SO_4 = 815
CO_3 = 36
Mg = <0.5
RS $CaCO_3$ = 74.2
RS $CaSO_4 \cdot 2H_2O$ = 0.67
Acid (0.14 gpm) 0.53 lpm
Cl = 167,000
87.2 lpm
(23.0 gpm)
Filter Press
Recycle Tank
Temp = 30°C
Ca = 1430
Na = 150
K = 14
pH = 12.3
Cl = 591
SO_4 = 814
CO_3 = 72
Mg = <0.5
RS $CaCO_3$ = 148
RS $CaSO_4 \cdot 2H_2O$ = 0.66
9.63 lpm
(2.54 gpm)
57.4 wt% solids
pH = 8.3
Ca = 1370
Mg = <0.5
Na = 157
K = 14
Temp = 30°C
Cl = 2040
SO_4 = 793
CO_3 = 45.6
RS $CaCO_3$ = 12.4
RS $CaSO_4 \cdot 2H_2O$ = 0.71
87.5 lpm
(23.1 gpm)

Concentrations in mg/l as ion except alkalinity which is in mg/l as $CaCO_3$. RS stands for relative saturation.

Figure 4-13. Summary of Pilot Unit Data from Test 5--Plant 9991.


pH = 9.9
Ca = 37
Mg = 0.9 Cl = 141
Na = 221 SO_4 = 286
K = 3.5 CO_3 = 78
RS $CaCO_3$ = 21.8
RS $CaSO_4 \cdot 2H_2O$ = 0.03
76.2 lpm (20.1 gpm)
Makeup Tank
19 lpm (5.0 gpm)
66.3 lpm (17.5 gpm)
95.1 lpm (25.1 gpm)
pH = 9.4 Cl = 146
Ca = 152 SO_4 = 660
Na = 237 CO_3 = 68
K = 5.8
RS $CaCO_3$ = 28.7
RS $CaSO_4 \cdot 2H_2O$ = 0.13
Ash 550 kg/hr (20.2 lb/min)
Mix Tank
8.8 wt% solids
Ca = 463 Cl = 148
Na = 280 SO_4 = 929
K = 9.4 CO_3 = 56
pH = 11.7
RS $CaCO_3$ = 92.3
RS $CaSO_4 \cdot 2H_2O$ = 0.45
Filter Press
10.6 lpm (2.8 gpm) 46.4 wt% solids
Acid (0.22 gpm) 0.83 lpm
Recycle Tank
Ca = 521 Cl = 153
Na = 282 SO_4 = 931
K = 12 CO_3 = 57
pH = 11.8
RS $CaCO_3$ = 96.6
RS $CaSO_4 \cdot 2H_2O$ = 0.48
85.3 lpm (22.5 gpm)
pH = 8.3
Ca = 480 Cl = 154
Na = 289 SO_4 = 1675
K = 12 CO_3 = 55
RS $CaCO_3$ = 5.9
RS $CaSO_4 \cdot 2H_2O$ = 0.81

Concentrations in mg/l as ion except alkalinity which is in mg/l as $CaCO_3$. RS stands for relative saturation.

Figure 4-14. Summary of Pilot Unit Data from Test 6--Plant 9991.

4.5.2.4 Summary of Test Results--

Results indicate that a significant portion of the transport water at Plant 9991 can be recycled without encountering gypsum scale formation. Lower ash levels in the slurry and use of hydrochloric acid for pH adjustment enable more transport water to be recycled before gypsum solubility limits are reached. Nearly 80 percent of the transport water was recycled at 5.9 weight percent fly ash and the gypsum relative saturation was only about 0.6. This indicates that additional water could have been recycled.

Only about 40 to 50 percent of the supersaturated calcium carbonate (average of 46 percent for the six tests) was precipitated in the system so that pH adjustment was necessary to desupersaturate calcium carbonate and avoid scale formation in the recycle line. However, use of sulfuric acid for pH adjustment significantly reduced the amount of transport water that could be recycled due to the increase in sulfate levels and the potential for gypsum scale formation.

Since calcium carbonate was slightly supersaturated in the recycled water, some scale formation may have been observed in longer-term tests. However, the relative saturations observed were all less than 20 after pH adjustment (except for Test 3). This is thought to be a relatively stable range at this pH with a relatively low concentration of either calcium or carbonate. Since calcium carbonate can be dissolved with an acidic solution, one potential option for fly ash systems may be periodic acid washing to remove calcium carbonate scale. This would eliminate the need for continuous sulfuric acid addition and reduce the potential for calcium sulfate scale formation. However, in bottom ash systems, this approach may not be appropriate since recycle water is frequently used to cool the refractory in the bottom ash hopper. In a bottom ash system, the cooling water is heated underneath the boiler and, since both calcium carbonate and gypsum are less soluble at higher temperatures, slightly supersaturated water can become more supersaturated. Scale can form and plug the cooling lines so that refractory cooling is lost and damage can result. Also, most refractories are sensitive to low pH so that acid washing may not be appropriate for all bottom ash systems.

4.5.3 Comparison of Pilot Unit Results and Process Model Simulations

The results of the pilot unit tests at Plant 9991 indicate that, for plants with a similar fly ash, an ash transport system with a 5 weight percent ash slurry which uses hydrochloric acid to adjust transport water pH is the design alternative which provides scale-free operation with the lowest blowdown rate. However, the minimum blowdown rate was not determined during pilot unit operations. In this section, the results of Test 4 with a 5 percent ash slurry using hydrochloric acid are compared with computer model predictions to verify the ability of the ash sluice model to simulate ash transport system operation. Then, the model is used to estimate the minimum blowdown rate from the fly ash transport system that can be achieved without scale formation.

The inputs to the ash sluice model are based on operating conditions observed in the pilot unit during Test 4. The inputs are summarized in Table 4-11.

The results predicted by the ash sluice model are compared to pilot unit performance in Table 4-12. In general, the blowdown composition predicted by the model compares very well with the values measured during the test. The concentrations of all the species except carbonate and sulfate predicted by the model are within 10 percent of the measured values and most are within 5 percent. However, the measured alkalinity value is nearly twice the predicted value. Potential sources of the carbonate discrepancy include one or more of the following: 1) errors in the alkalinity measurements, 2) absorption of CO_2 from the atmosphere in the pH adjust tank, 3) errors in the estimated approach of supersaturated calcium carbonate to equilibrium, which was input to the model, and 4) observed fluctuations in the pH of transport water in the pilot plant pH adjust tank and the resulting significant impact on pH and alkalinity.

The calcium carbonate relative saturation calculated for pilot unit data is higher than predicted due to the higher carbonate values measured in the pilot unit blowdown stream. The difference between the relative saturations

TABLE 4-11. SUMMARY OF INPUTS TO THE ASH SLUICE MODEL TO SIMULATE TEST 4 OPERATING CONDITIONS

Variable	Specified Value
Ash slurry, weight percent	5.9
Makeup water quality, mg/l as ion	
Ca	18.0
Mg	0.7
Na	119.0
K	1.0
Cl	37.0
Alkalinity (as $CaCO_3$)	92.0
SO_4	98.0
HCl acid addition based on recycle water pH	8.4
Ash leachability, mg/g ash	
Ca	7.15
Mg	0.00
Na	0.40
K	0.04
Cl	0.00
SO_4	2.64
Blowdown rate, lpm (gpm)	28.8 (7.59)
Solids in dewatered ash, weight percent	58
Pond water temperature, °C (°F)	28 (82)
Net annual evaporation	None
Approach of supersaturated $CaCO_3$ to equilibrium, percent	46

TABLE 4-12. COMPARISON OF ASH SLUICE MODEL PREDICTIONS WITH PILOT UNIT PERFORMANCE FOR TEST 4

	Predicted by Model	Measured in Pilot Unit	Difference (Percent)
System Blowdown Composition			
Component, ppm as ion			
Ca	1650	1700	3
Mg	0.2	<0.5	N/A[a]
Na	186	197	6
K	9.6	10	4
Cl	2670	2740	3
Alkalinity (as $CaCO_3$)	14.8	30	50
SO_4	722	647	-12
pH	8.4[b]	8.4	0
Relative Saturation			
$CaCO_3$	4.8	11.9[c]	150
Gypsum	0.68	0.62[c]	-9
System Flow Rates, lpm (gpm)			
Hydrochloric acid	0.796 (0.21)	1.02 (0.27)	22
Makeup	33.7 (8.9)	34.9 (9.2)	3
Sludge (water loss)	5.68 (1.5)	6.06 (1.6)	6

[a] N/A - Not Applicable

[b] Specified as model input.

[c] Calculated based on measured composition.

is not significant with respect to an actual operating system since the carbonate value is so small that no appreciable amount of scale could precipitate from solution. The gypsum relative saturations compare very well.

The flow rates also compare very well. The biggest difference is the acid flow rate. However, the acid flow rate is very small, and it was difficult to obtain accurate measurements at those levels. Comparison of the measured and predicted chloride levels are within 3 percent which indicates that the model can accurately estimate hydrochloric acid addition rates.

Overall, the ash sluice model was demonstrated to adequately predict pilot unit performance. The ash sluice model was then used to predict the reduction in blowdown that could be achieved without gypsum scale formation since the relative saturation of calcium carbonate could be controlled by adjusting the pH. The same model inputs that were presented earlier in Table 4-11 were used to simulate operation at reduced blowdown rates.

The results of the minimum blowdown simulation are compared to the simulation of Test 4 in Table 4-13. The results indicate that as the liquid blowdown is reduced from 29 lpm (7.6 gpm) to 7.6 lpm (2.0 gpm), the relative saturation of gypsum increases from 0.68 to 1.1. The total blowdown from the system includes liquid blowdown and water occluded with the dewatered ash (sludge). The total blowdown was reduced from 34 lpm (9.1 gpm) to 13 lpm (3.5 gpm). At maximum recycle, approximately 94 percent of the transport water can be recycled after ash dewatering. Therefore, most of the transport water can be recycled, but closed-loop operation cannot be obtained without the potential for gypsum scale formation to occur in the recycle line. In fact, some safety margin should be provided to allow reliable operation to be maintained during process upsets and fluctuations in ash and makeup water compositions. Therefore, a blowdown rate somewhat greater than the minimum calculated rate would be recommended.

TABLE 4-13. COMPARISON OF MINIMUM BLOWDOWN SIMULATION WITH SIMULATION OF TEST 4

	Model Predicted Minimum Blowdown		Pilot Unit Test 4	
System Blowdown Composition				
Component, ppm as ion				
Ca	3910		1650	
Mg	0.1		0.2	
Na	343		186	
K	23.8		9.6	
Cl	6695		2670	
Alkalinity (as CaCO$_3$)	7.5		14.8	
SO$_4$	1036		722	
pH	8.4[a]		8.4	
Relative Saturation				
CaCO$_3$	3.1		4.8[b]	
Gypsum	1.1		0.68[b]	
System Flow Rates, lpm (gpm)				
Hydrochloric Acid	0.796	(0.21)	0.796	(0.21)
Makeup	12.5	(3.3)	33.7	(8.9)
Sludge (water loss)	5.68	(1.5)	5.68	(1.5)
Liquid Blowdown	7.58	(2.0)	28.8	(7.6)
Total Blowdown	13.3	(3.5)	34.5	(9.1)

[a] Specified as model input.

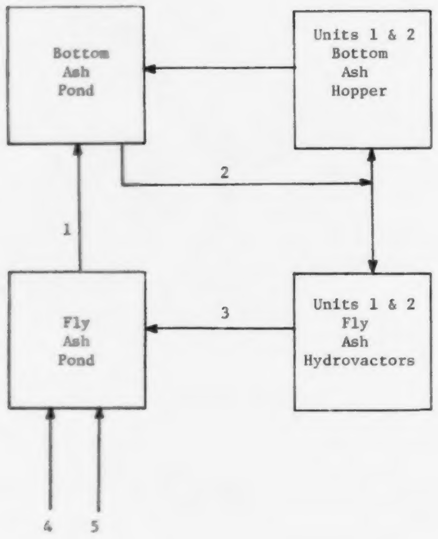
[b] Calculated based on measured composition.

4.5.4 Application of Testing Results to Plant 9991

In Plant 9991, fly ash and bottom ash transport systems use a common source for sluice water. A schematic diagram of the plant ash transport system is presented in Figure 4-15 along with characteristics of the process streams. Makeup water enters the fly ash pond which discharges to the bottom ash pond. Transport water for sluicing both bottom and fly ash is obtained from the bottom ash pond. Therefore, the chemistry of the two ash systems is closely interrelated.

The analytical results of samples obtained at the plant in August 1982 are also summarized in Figure 4-15. At that time, water had not been discharged from the ponds. These data indicate that the concentrations of species are considerably less than the concentrations encountered during most of the pilot unit tests when blowdown was discharged from the unit. As a result, the gypsum relative saturations in the ponds are lower than encountered in the pilot unit. The data collected to characterize the full-scale system later in the year during pilot unit testing are similar to the data presented in Figure 4-15. These results indicate that the chemistry of the ash handling system at Plant 9991 has not reached steady-state operation and the concentrations of species in the ponds will continue to increase over a period of time. Since the ponds are relatively large and the units are used in load peaking service, several years could be required to reach steady-state operation.

Nevertheless, calcium carbonate scale has been observed at the plant. The scale has plugged strainer screens for the return water pumps. The relative saturation of calcium carbonate in the return water is 17.5 for the data summarized in Figure 4-15. Ultimately, gypsum scale formation could also occur in the return line if closed-loop operation is maintained. Scaling problems could become more severe in the bottom ash system where return water is used to cool the refractory in the bottom ash hopper. Since both calcium carbonate and gypsum are less soluble at higher temperatures, the cooling water lines could become plugged with scale as the temperature of the cooling water increases underneath the boiler.


Bottom
Ash
Pond
Units 1 & 2
Bottom
Ash
Hopper
2
1
Fly
Ash
Pond
3
Units 1 & 2
Fly
Ash
Hydrovactors
4
5

	Process Stream				
Species, mg/l	1-Fly Ash Pond Overflow	2-Sluice Water Return	3-Fly Ash Discharge	4-Treated Wastewater	5-Coal Pile Runoff
Calcium	220	131	450	67	86
Magnesium	2.3	2.4	7.9	1.1	4.5
Sodium	80.0	77.0	110	65.0	56
Potassium	3.1	3.4	5.3	1.4	1.8
Chloride	37.0	38	51	38	31
Carbonate	12.8	13.6	13.8	81.0	68.3
Sulfate	420	285	530	194	280
Silica	13.7	14.1	11.6	6.4	6.6
pH	10.4	10.4	11.3	8.1	8.9
Temperature, °F	82	88	88	100.2	89
Relative Saturation					
Calcium Carbonate	17.3	17.5	26.6	2.8	11.0
Gypsum	0.2	0.1	0.3	0.05	0.07
Magnesium Hydroxide	0.3	0.6	74.0	-	-
CO_2 Partial Pressure, atm	6.5×10^{-8}	8.9×10^{-8}	7.7×10^{-19}	7.5×10^{-4}	8.0×10^{-5}

Figure 4-15. Schematic Flow Diagram and Chemical Characterization of Plant 9991 Ash Handling System.

Use of acid addition to adjust the pH of the return water should be effective in controlling calcium carbonate scale formation at Plant 9991. Use of hydrochloric acid instead of sulfuric acid would lengthen the time period before the system becomes supersaturated with respect to gypsum. However, gypsum scale is expected to eventually occur in either case if there is no blowdown from the system.

If closed-loop operation is maintained at Plant 9991 over a long period of time, another treatment approach is expected to be required eventually to control gypsum scale formation. Alternatively, blowdown from the system would be an effective method of controlling gypsum scale formation. A larger blowdown rate would be required if sulfuric acid is used for pH adjustment instead of hydrochloric acid. Although hydrochloric acid is more expensive than sulfuric acid, lower blowdown rates achievable with hydrochloric acid could reduce acid consumption. Nevertheless, a more detailed analysis would be required to identify the most cost-effective treatment approach.

Requirements for liquid phase blowdown rates would also be affected by the amount of water occluded with the ash. The weight percent solids in the sludge in the ponds could not be determined by the field team. Since the dewatering equipment used in the pilot unit (filter press) may produce higher weight percent solids in sludge than the solids settling in a full-scale system (settling ponds), differences in water occluded with the ash could impact liquid phase blowdown requirements.

One of the parameters considered by the model is the amount of CO_2 transfer between the atmosphere and ash ponds. The pilot unit was not equipped to evaluate this phenomenon since filter presses were used to dewater the fly ash and the water received only limited exposure to the atmosphere. However, samples of the full-scale system provided some input in evaluating the significance of CO_2 transfer in the ash ponds.

In the model, CO_2 transfer is estimated based on the calculated CO_2 partial pressure in the ash pond water versus the CO_2 partial pressure in the atmosphere to determine if a driving force exists to absorb or desorb CO_2 in the pond. Since the model is not currently capable of estimating the exact amount of CO_2 transfer, two cases are typically considered in simulations to evaluate the range of conditions that can be encountered: 1) no CO_2 transfer occurs or 2) CO_2 is in equilibrium between the ash ponds and atmosphere.

Calculated CO_2 partial pressures in the ash handling system for Plant 9991 are presented in Figure 4-15. The partial pressures in the fly ash and bottom ash ponds are 6.6×10^{-3} and 8.8×10^{-3} Pa (6.5×10^{-8} and 8.7×10^{-8} atmospheres), respectively. This indicates that a significant driving force exists for the alkaline ash ponds to absorb more acid CO_2 from the atmosphere (CO_2 partial pressure in the atmosphere is about 33 Pa). Therefore, not enough CO_2 transfer was observed at Plant 9991 to approach equilibrium conditions. While some CO_2 may have been absorbed, the data are not adequate to estimate the quantity by material balance since absorbed CO_2 could have precipitated as calcium carbonate in the ash ponds.

Based on the data from Plant 9991, the most appropriate assumption to use in the model until more data are available is that no CO_2 transfer occurs. This assumption also tends to be more conservative for estimating treatment requirements for systems with alkaline ash.

SECTION 5

ANALYTICAL DATA QUALITY

As part of the ash sluice test program, Radian performed chemical characterizations of the pilot and host site ash sluice systems. This was done by collection and analysis of process stream samples from both systems. The analytical data were used along with other process data to calculate the quantity of material leaching from the ash, the amount of CO_2 transfer in the system, and the degree of precipitation of supersaturated species occurring in the pond. The values obtained were used as input to the ash sluice process model. The validity of conclusions based on the pilot unit testing is therefore dependent, in part, upon the quality of the analytical data.

The QA/QC program described in the Quality Assurance Project Plan (Appendix H) served two major purposes with respect to analytical data quality. First, QC procedures and acceptance criteria were specified to ensure that precision and accuracy of the analytical data were within prescribed limits. Thus, the QC procedures served a control function in this respect. Second, in addition to the control function, certain QA and QC procedures were used to provide a basis for assessment of the quality of the analytical data which were generated. This section discusses these assessment techniques and presents estimates of precision and accuracy for various analyses based on QA/QC results.

5.1 SUMMARY OF RESULTS

Performance audit results and quality control data for the major analytical parameters (anions, cations, hardness, alkalinity, pH, and conductivity) indicated that precision and accuracy of these analyses were adequate to generate measurement data of acceptable quality.

Prior to field testing, a quality assurance plan was prepared which presented estimated precision and accuracy objectives for each measurement parameter. Table 5-1 presents these estimates along with measured values for precision and accuracy based on control sample analyses and performance audit results. For four parameters, sodium, magnesium, potassium, and alkalinity, audit results indicated relative error greater than the estimated accuracy. Measured precisions (repeatability) for sulfate, sodium, and calcium analyses parameters were less (i.e., the relative variabilities were greater) than estimated. However, the magnitude of the differences between estimated and measured precision and accuracy, when considered in the context of the process sample results, did not appreciably affect the adequacy of the measurement data. Precision (repeatability, or day-to-day variability) for all parameters, based on control sample analyses, was better than 5 percent, which is typically considered to be very good. Precision estimates of 2-3 percent were, perhaps, somewhat optimistic. In the instances where measured accuracy was not as good as predicted, the absolute error which these values represent was actually quite small. Potassium audit results, for example, indicated a mean relative error of 18.8 percent. However, the true concentrations of the two audit samples were 1.7 and 7.1 mg/1. A relative error of 18.8 percent at a concentration of 7.1 mg/1 represents an absolute error of only 1.3 mg/1.

5.2 DATA QUALITY ASSESSMENT

The precision and accuracy estimates presented in Table 5-1 were based upon performance audit results and internal QC data. The procedures used to collect and evaluate these data, along with detailed results for the various methods, are presented and discussed in this section.

5.2.1 Methods of Quantitating Data Quality

The performance audits and QC analyses conducted during the ash sluice pilot unit test program were designed to provide a quantitative assessment of the analytical data quality. The two aspects of data quality which are of primary concern are precision and accuracy. Accuracy reflects the degree to

TABLE 5-1. SUMMARY OF ESTIMATED VS. MEASURED PRECISION AND ACCURACY

Parameter	Method	Accuracy [a]		Precision [c]	
		Estimated	Measured [b]	Estimated	Measured [d]
Sulfate	Ion Chromatography	±5%	-4.8%	3%	3.6%
Chloride	Ion Chromatography	±5%	+3.2%	3%	2.7%
Sodium	Atomic Absorption	±5%	+5.9%	2%	4.3%
Calcium	Atomic Absorption	±5%	+2.2%	2%	2.7%
Magnesium	Atomic Absorption	±5%	-11.2%	4%	2.5%
Potassium	Atomic Absorption	±5%	+18.8%	5%	3.0%
Hardness	Titrimetric	±5%	+3.5%	3%	1.8%
Alkalinity	Titrimetric	±5%	+1.8% [e]	5%	0.4%
Conductivity	Potentiometric	±5%	-0.9%	6%	---
pH	Potentiometric	±1%	+0.1%	3%	---

[a] Relative error, percent.

[b] Based on audit sample analyses.

[c] Coefficient of variation, CV, where $CV = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100$.

[d] Repeatability, based on control sample analyses.

[e] Based on audit sample B results only; actual concentration of sample A was below the limit of quantitation for the method, and the results are therefore considered invalid.

which the measured value represents the actual or "true" value for a given parameter, and includes elements of both bias and precision. Precision is a measure of the variability associated with the measurement system as a whole (i.e., procedures, analysts, instrumentation).

The data necessary for assessment of precision and accuracy were obtained in several ways. The performance audits for the various measurement parameters were meant to measure accuracy of the measurement systems and consisted of submitting audit samples for analysis by the various methods used for field sample analyses. Variability (precision) associated with the various measurement systems was measured and documented using QC procedures such as control sample analyses and duplicate analyses. Extrapolation of the audit and QC data to actual samples and measurements provides the primary mechanism whereby error limits for various measurements may be estimated and the confidence in the measurement data defined. Audit and QC procedures are discussed in more detail in subsequent sections.

The audit data presented in this section are summarized in terms of "relative error." This reflects the degree to which the measured value agrees with the actual value, in terms of percent of the actual value:

$$\text{Relative error} = \frac{\text{Measured value} - \text{Actual value}}{\text{Actual value}} \times 100\% \qquad (5\text{-}1)$$

This way of expressing accuracy allowed for a comparison of accuracy at different levels (e.g., different concentrations) and for different parameters of the same type (e.g., different compounds analyzed by the same method). In summarizing the audit results, mean relative errors are presented for each parameter.

The QC analyses results are useful in providing a quantitative assessment of analytical data quality with respect to precision. Replicate samples and replicate analyses were used to measure and document the variability (precision) associated with the various measurements. Precision is a measure of mutual agreement between independent measurements of the same property, made under prescribed similar conditions. Various measures of precision (replicability, repeatability, and reproducibility) exist depending upon these "prescribed similar conditions." Replicability is a measure of variability among replicate analyses. For repeatability, the same sample is analyzed by the same laboratory, but on different days. Repeatability, for this study, is therefore a measure of day-to-day variability.

Analytical variability, or precision of the measurement, is typically expressed in terms of the coefficient of variation (CV) for replicates, where:

$$CV = \frac{\text{Standard Deviation}}{\text{Mean}} \times 100\% \qquad (5\text{-}2)$$

The CV is in percent since it is the standard deviation of a set of measurements expressed as percent of their mean (relative standard deviation). Precision of analytical data is commonly reported in terms of the CV when the standard deviation tends to depend on the level of the measurement. All precision estimates presented in this section are expressed in terms of CV.

When individual CV values were combined (pooled) to obtain an overall average measure of variability for a given type of analysis or measurement, the following technique was used:

$$\text{Pooled CV} = \sqrt{\frac{\sum_{i=1}^{n} X_i^2 \, DF_i}{\sum_{i=1}^{n} DFi}} \qquad (5\text{-}3)$$

where:

X_i = CV of data set i (e.g., CV for one duplicate pair, i),

DF_i = degrees of freedom for data set i (k_i-1),

n = total number of data sets (e.g., total number of duplicate pairs),

k_i = number of data points in set i (e.g., k=2 for duplicates)

i = data set 1,2,3,...n

5.2.2 Performance Audit Results

The performance audit for this program addressed 10 analytical parameters. Of these, average results for six were within accuracy limit estimates (±5 percent, except for pH, which was +1 percent) presented in the QA project plan. Mean relative error (average accuracy) for total alkalinity, magnesium, potassium, and sodium exceeded the estimated accuracy of ±5 percent, based on audit results. Performance audit results for all parameters are presented in Table 5-2. "Typical" process sample concentration ranges for each parameter are presented for comparison to audit sample concentrations.

As indicated in Table 5-2, each parameter was audited at two concentration levels. The audit consisted of submitting EPA Water Pollution Quality Control Check Samples, Mineral (WP 478) for analysis along with pilot unit samples. Although there was significant disparity between audit sample concentrations and process sample concentrations for several parameters (e.g., hardness, alkalinity, and calcium), certified audit samples having more representative concentrations for the parameters of interest were not available from the EPA. Audit sample concentrations for some parameters were substantially lower than concentrations typically seen in the process samples. In these cases the audit results are probably not representative of analytical accuracy for the process samples with respect to relative error, since errors which may be very small in comparison to process concentrations appear quite large when expressed as a percentage of the audit sample concentration. Considering the analytical methods used, it is not necessarily a valid conclusion to expect similarly large relative errors at much higher concentrations. Rather, in these cases, the audit results are probably more indicative of the

TABLE 5-2. PERFORMANCE AUDIT RESULTS

Parameter	Range of "Typical" Process Concentrations	Sample A				Sample B				Mean Relative Error (%)
		Actual Value	Measured Value	Error[a]	Relative Error[b] (%)	Actual Value	Measured Value	Error[a]	Relative Error[b] (%)	
pH	8-12	7.4	7.5	0.1	+1.4	8.6	8.5	-0.1	-1.2	+0.1
Sp. Conductance (µmhos)	—	125	124	1	-0.8	479	474	-5	-1.0	-0.9
Total Hardness (mg/L $CaCO_3$)	300-4000	26.6	28.0	1.4	+5.3	109	107	-2	-1.8	-3.5
Total Alkalinity (mg/L $CaCO_3$)	300-2500	16.0	20.0	4.0[c]	+25[c]	73.7	75.0	1.3	+1.8	+1.8[c]
Calcium (mg/L)	300-1700	6.7	7.0	0.3	+4.5	32.0	32.0	0.0	0	+2.2
Magnesium (mg/L)	ND-2	2.4	2.2	-0.2	-8.3	7.1	6.1	1.0	-14	-11.2
Potassium (mg/L)	2-12	1.7	2.2	0.5	+29	7.2	7.8	0.6	+8.3	+18.8
Sodium (mg/L)	150-250	7.0	6.6	0.4	-5.7	40.0	47.0	7.0	+17.5	+5.9
Chloride (mg/L)	30-2000	20.5	21.0	0.5	+2.4	70.2	73.0	2.8	+4.0	+3.2
Sulfate (mg/L)	100-3000	12.0	11.0	-1.0	-8.3	75.0	74.0	1.0	-1.3	-4.8

[a] Difference between measured value and actual value.

[b] Difference between measured value and actual value expressed as a percentage of the mean.

[c] Actual concentration of sample A was less than limit of quantitation (20 mg/l) for the method used; results not considered valid and not used in calculating mean relative error.

absolute magnitude of analytical error than relative magnitude. For example, consider the results for total hardness. The relative error of 5.3 percent indicated for audit sample A represents an absolute error of only 1.4 mg/l $CaCO_3$. Typical process concentrations ranged from about 300 mg/l to 4000 mg/l. At 300 mg/l an error of 1.4 mg/l represents a relative error of only 0.5 percent. For sample B, at a true concentration of 109 mg/l, absolute error was -2 mg/l or -1.8 percent. These data suggest that accuracy of the process sample hardness analyses was probably well within the ±5 percent estimate. For potassium and magnesium, on the other hand, the audit sample concentrations were much closer to typical sample concentrations and the mean relative error for the audit samples is a reasonable estimate of relative accuracy for these parameters. For these species, estimated accuracy of ±5 percent was somewhat optimistic for the low concentrations seen in the process samples. These examples illustrate the importance of considering audit results in the context of the measurement data. Taken out of this context, it is difficult to use them to draw meaningful conclusions about the measurement data.

5.2.3 Quality Control Results

Two of the internal QC procedures associated with the process sample analyses provide a basis for assessing analytical precision. Duplicate sample analyses may be used to estimate precision in terms of replicability, while QC sample analyses and repeat sample analyses provide a basis for estimating day-to-day variability (repeatability). Overall, analytical precision was excellent, with CV's less than 5 percent except in two cases. Detailed results are presented below.

5.2.3.1 Replicability--

In order to estimate the analytical variability among samples analyzed on the same day, the results of replicate analyses can be compared. Replicate analyses are independent determinations of multiple aliquots of the same sample, by the same analyst, at essentially the same time and same conditions. Table 5-3 presents results of duplicate analyses for hardness, total alkalinity, cations, and anions. Precision (replicability) was typically better

TABLE 5-3. RESULTS OF DUPLICATE ANALYSES--REPLICABILITY

Parameter	Method	Sample ID	Mean Conc.	CV (%)	Pooled CV
Sulfate	Ion Chromatography	1143	144	6.4	3.1
		1103	178	4.0	
		1144	417	0	
		1151	212	0	
		1143	143	5.4	
		1147	610	0.9	
		1182	2696	0.3	
		1260	405	0.2	
		1257	289	0.5	
Chloride	Ion Chromatography	1143	160	4.9	1.9
		1103	288	1.7	
		1144	157	0	
		1151	28	0	
		1143	154	0.5	
		1147	151	0.9	
		1182	75	0.9	
		1260	38	1.9	
		1257	38	0	
Sodium	Atomic Absorption	1055	183	0	1.8
		1058	223	1.3	
		1059	246	2.3	
		1144	214	0	
		1075	85	3.3	
		1142	237	0	
		1190	200	0.7	
		1182	189	2.6	

(Continued)

TABLE 5-3. (Continued)

Parameter	Method	Sample ID	Mean Conc.	CV (%)	Pooled CV
Calcium	Atomic Absorption	1006	379	0.4	0.9
		1144	458	1.1	
		1142	751	1.2	
		1182	1019	0.4	
Magnesium	Atomic Absorption	1006	0.53	1.3	1.3
Potassium	Atomic Absorption	1144	3.8	1.9	1.4
		1142	4.5	1.6	
		1182	11.0	0	
Hardness	Titrimetric	1022	37	13.4	5.2
		1027	1976	0.4	
		1014	311	2.7	
		1078	549	0.3	
		1115	328	0.2	
		1119	582	0.5	
		1168	2271	0.1	
Alkalinity	Titrimetric	1005	428	0	1.0
		1011	308	0.9	
		1076	497	0.6	
		1142	1755	0.4	
		1147	2389	0.1	
		1153	1030	0.1	
		1320	86	2.5	

than 5 percent, with two exceptions. In the two cases where the CV was greater than 5 percent (sample No. 1143, sulfate, and sample No. 1022, hardness), the measured values were lower than average. This is especially noticeable for the hardness analyses for sample No. 1022, where the mean measured value was nearly 10 times lower than that of the next lowest value for the duplicate samples. If sample No. 1022 is omitted, the pooled CV for hardness analyses becomes 1.2 percent, rather than 5.2 percent.

5.2.3.2 Repeatability--

Day-to-day variability (repeatability) was measured by making independent analyses of the same process sample at the same laboratory on different days. This measure of precision is a somewhat more conservative estimate than replicability since day-to-day variability includes variability associated with calibration. Even considering this additional source of measurement variability, overall variability was very good at less than 5 percent (CV) for all parameters considered (anions, cations, hardness, and alkalinity).

For anion and cation analyses, two solutions were used as control samples. These solutions contained the species of interest at two concentrations, "high" and "low." Analyte concentrations in the high level QC sample were approximately two times those of the low level QC sample. In addition to these, a third QC sample was used for chloride, sulfate, and sodium analyses. This sample was similar to the other two, but was made to more closely resemble the matrix of the process samples, with respect to concentrations of both major and minor species. This QC sample is referred to as the "matrix" sample. A single control sample was used for hardness and alkalinity analyses. Table 5-4 summarizes results of the control sample analyses.

Results for the high and low QC sample analyses for each parameter were plotted in the form of control charts. Example control charts for sulfate are shown in Figure 5-1. Control charts for the other parameters are presented in Appendix C. The solid line on each chart represents the mean measured concentration. The two dashed lines represent the upper and lower warning limits, based on the estimated precision for each parameter.

TABLE 5-4. DAY-TO-DAY VARIABILITY (REPEATABILITY)

Parameter	Method	Control Standard	Number of days	Mean Conc. (mg/L)	CV (%)	Pooled CV
Sulfate	Ion Chromatography	Low QC	6	1714	1.8	3.6
		High QC	8	4036	4.7	
		Matrix	3	508	2.7	
Chloride	Ion Chromatography	Low QC	6	368	1.4	2.7
		High QC	8	771	2.8	
		Matrix	4	357	3.8	
Sodium	Atomic Absorption	Low QC	14	41	4.8	4.3
		High QC	13	77	3.8	
		Matrix	3	189	3.5	
Calcium	Atomic Absorption	Low QC	6	122	2.9	2.7
		High QC	8	264	2.6	
Magnesium	Atomic Absorption	Low QC	5	17	2.6	2.5
		High QC	7	33	2.5	
Potassium	Atomic Absorption	Low QC	4	71	4.2	3.0
		High QC	7	155	2.2	
Hardness	Titrimetric	QC-H	18	250	1.8	1.8
Alkalinity	Titrimetric	QC-A	14	252	0.4	0.4

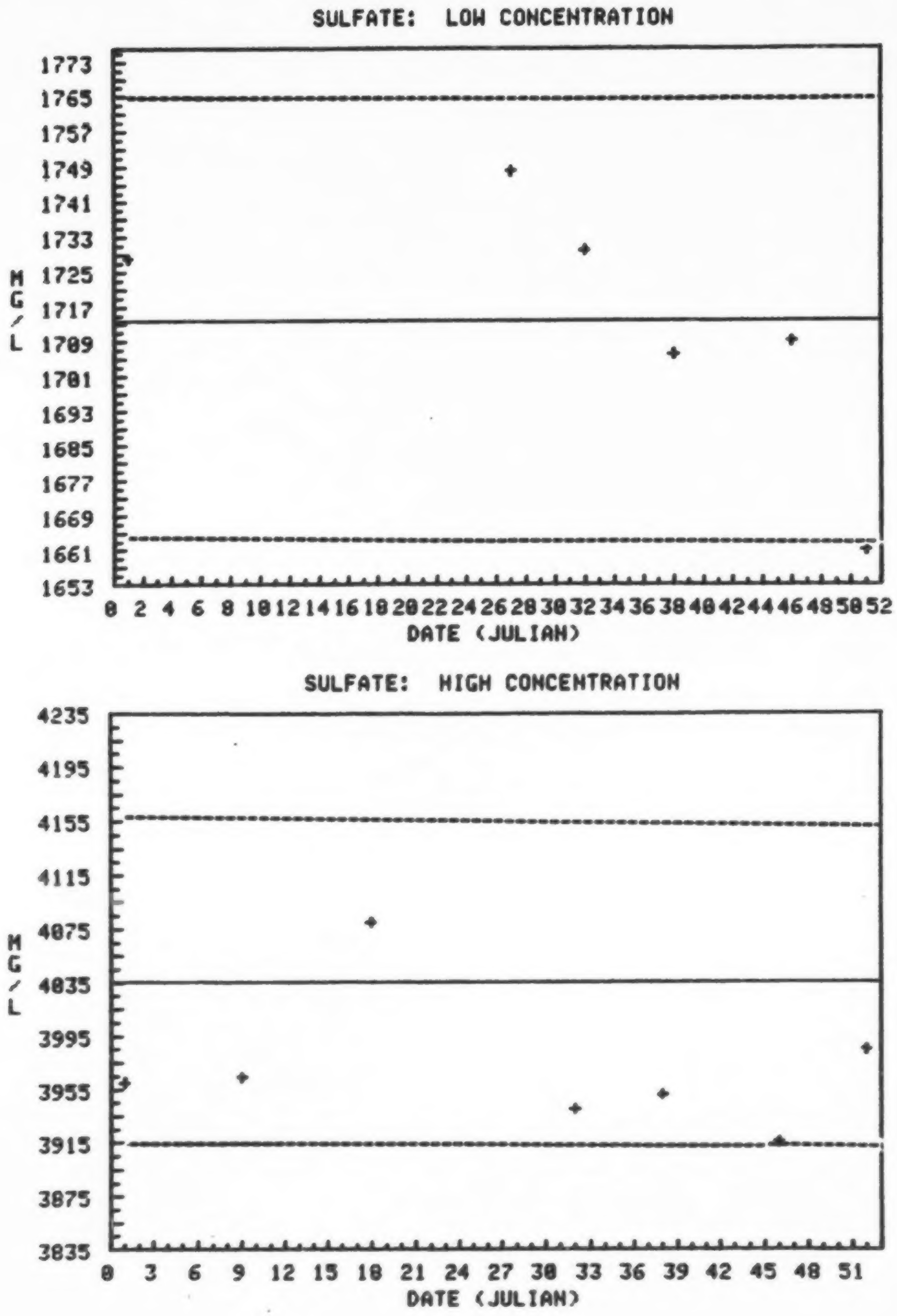


Figure 5-1. Example Control Charts for Sulfate QC Samples.

SECTION 6

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